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CHEMISTRY OF PROCESSIBLE ACETYLENE-TERMINATED IMIDES

Hughes Aircraft Company
E-O and Data Systems Group
El Segundo, CA 90245

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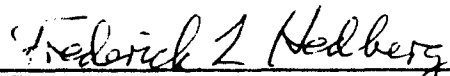
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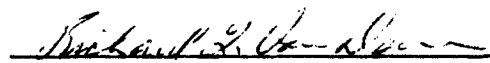
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chemistry was then applied successfully to the preparation of a series of lower cost acetylene terminated isoimides by substitution of 4,4'-oxydianiline for the 1,3-bis (3-aminophenoxy) benzene. The resultant resins were found to be curable at 316°C to crosslinked imides with Tg values in excess of 316°C for oligomer lengths of 1, 2 and 3. Thermal and mechanical studies were carried out on all of the resins.

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FOREWORD

This final report was prepared by the Materials Technology Department in the Technology Support Division, Electro-Optical and Data Systems Group of Hughes Aircraft Company, El Segundo, California 90245, under Air Force Contract F33615-82-C-5016, "Chemistry of Processible Acetylene-Terminated Imides." the program was sponsored by the Air Force Wright Aeronautical Laboratory, Polymer Branch, with Dr. Frederick L. Hedberg as the Project Monitor.

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The processes contained in this report have either patents issued or patents pending to Hughes Aircraft Co.

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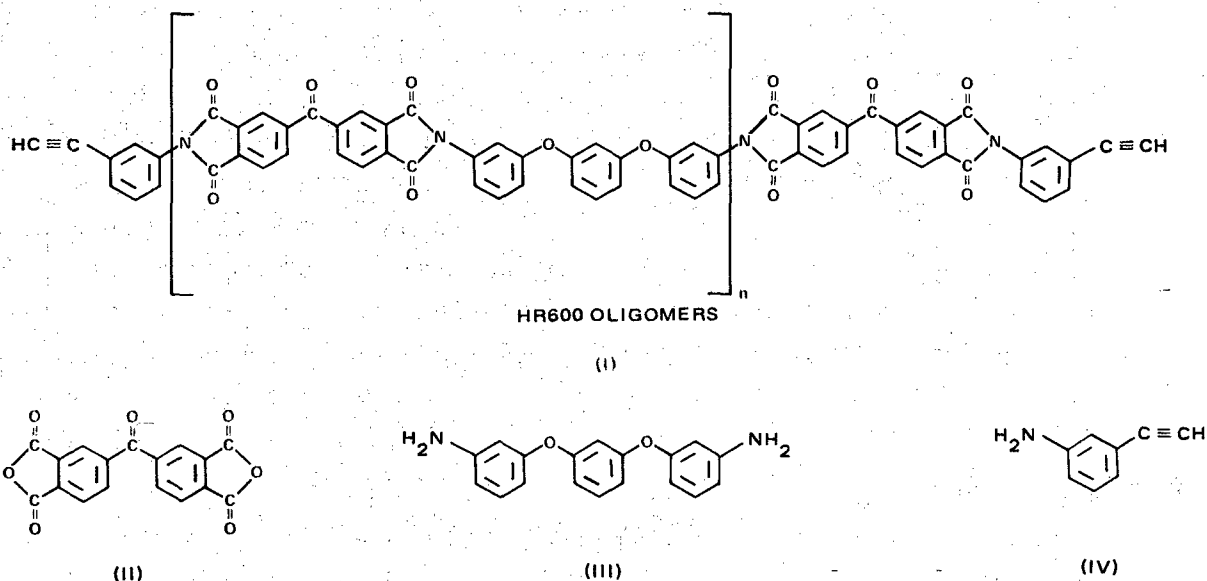
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1.0 INTRODUCTION

Research was initiated in the early sixties, under the sponsorship of the U.S. Air Force Wright Aeronautical Materials Laboratory (References 1-7), to develop high temperature resins which cure by addition reactions, for composites and adhesive applications. A unique system of resins was developed based on the thermally induced homopolymerization of acetylene. The oligomers are difunctional acetylene-terminated polyimides. They are sufficiently low in molecular weight and have the necessary structural features to impart solubility and fusibility during processing.

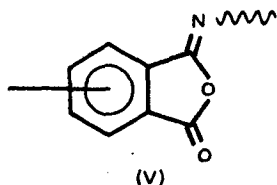
Polyimides have excellent thermal and thermo-oxidative stability but in general tend to be insoluble and intractable. Even as low molecular weight prepolymers special considerations have to be given to the polymer backbones to impart fusibility and solubility to the acetylene-terminated polyimide prepolymer. Numerous combinations of aryl diamines, difunctional aromatic acid anhydrides and 3-aminophenylacetylene were investigated concerning the processing characteristics imparted to the oligomer. A family of oligomers known as HR600 (See Structure I), having reasonably good processibility was finally prepared using the



monomers, benzophenonetetracarboxylic dianhydride (BTDA) (see Structure II), 1,3-bis (3-aminophenoxy)benzene (APB) (see Structure III) and 3-aminophenylacetylene (APA) (See Structure IV).

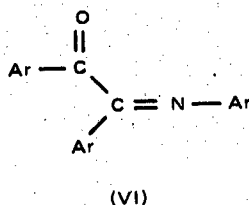
The oligomer with a value of $n = 1$ is also referred to as having a degree of polymerization (DP) of one. This oligomer was prepared by the reaction of BTDA, APB and APA in a molar ratio of 2:1:2. By adjusting the molar ratio of the reactants, the value n and DP could be varied. In practice, the range of values for the DP was limited because processibility of the oligomer rapidly decreased as the DP increased. The oligomer with a DP of one was found to be very promising, both as a molding and as a matrix resin. This oligomer was initially licensed to the Gulf Oil Chemical Company and marketed under the trade name Thermid 600. Recently, it was relicensed to National Starch and Chemical Company. Thermid 600 has found utility as matrix resin for glass and graphite-reinforced composites, chopped graphite-reinforced molding compounds, adhesives for titanium, self-lubricating composites, bearing retainers, adhesives for other polyimides such as Kapton, and matrix resin for printed wiring boards. Furthermore, Thermid 600 has the proven ability to meet both long term (under 550°F), and short term exposure (over 550°F), with minimal deterioration of mechanical properties. However, these resins have had limited acceptability because their high melting point and rapid cure allow a very limited time at viscosities acceptable for processing (i.e., having a narrow "processing window"). The processing window becomes even smaller with higher DP oligomers. Furthermore, these resins have a relatively limited solubility in common solvents. Different approaches have been tried to improve the processibility of these oligomers. The use of acetylene-terminated reactive diluents during processing met with limited success because of the general lack of mutual solubility of the oligomer and the diluent.

Recently, enhanced processibility was achieved for these oligomers without compromising the ultimate thermal and thermo-oxidative stability of the resins by using the isomeric form of the imide. This isomeric form, commonly known as an iminolactone or an isoimide (see Structure V), was first reported nearly 100 years ago (Reference 8), but little attention was paid to compounds until 1961 (References 9-13, 15).



When the physical properties of the isoimide were compared to the analogous imide, the isoimide was generally found to have a much lower melting point (Reference 14), and was much more soluble in a variety of solvents. This structure is metastable and can be readily converted irreversibly to the imide form, either thermally or catalytically. Although Structure

V shows a five-membered ring, the literature also reports acyclic isoimides (References 16-19), characterized by Structure VI



where Ar denotes aryl groups. Acyclic isoimides are even more metastable than the cyclic structures. Isoimides can be readily converted to the isomeric imide structures through catalysis such as acetic anhydride—sodium acetate at 65–100°C, benzenetriethylammonium acetate at reflux temperature, dioxane-acetic acid at 65°C, and refluxing acetic acid. It can be generally inferred that nucleophilic catalysts promote the isoimide-to-imide conversion.

The formation of the cyclic isoimide structure is through the cyclodehydration of the amic acid precursor by selected chemical reagents. Generally, chemical dehydration of N-substituted amic acids gives varying ratios of imide and isoimides, depending on the reaction conditions employed, the nature of the amic acid and the chemical reagent used. Thermal cyclodehydration invariably yields the imide structure (Figure 1). A number of common chemical dehydrating agents are known to be effective in converting amic acids to imides (References 13, 20–26). However, very few reagents are reported to dehydrate amic acid to isoimide (References 10, 26–31).

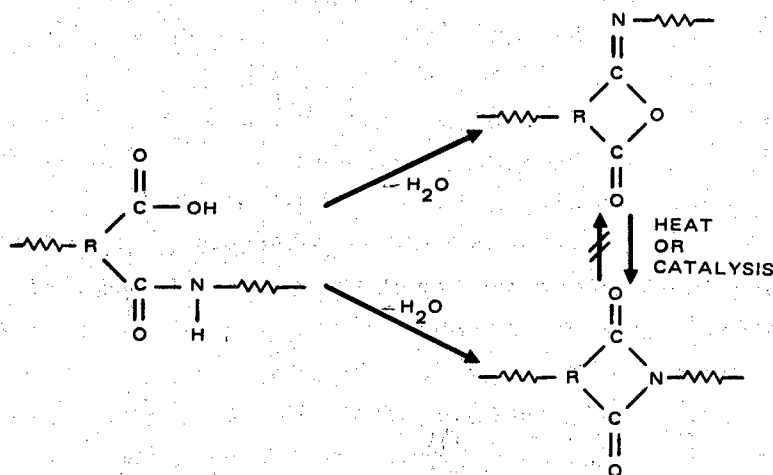
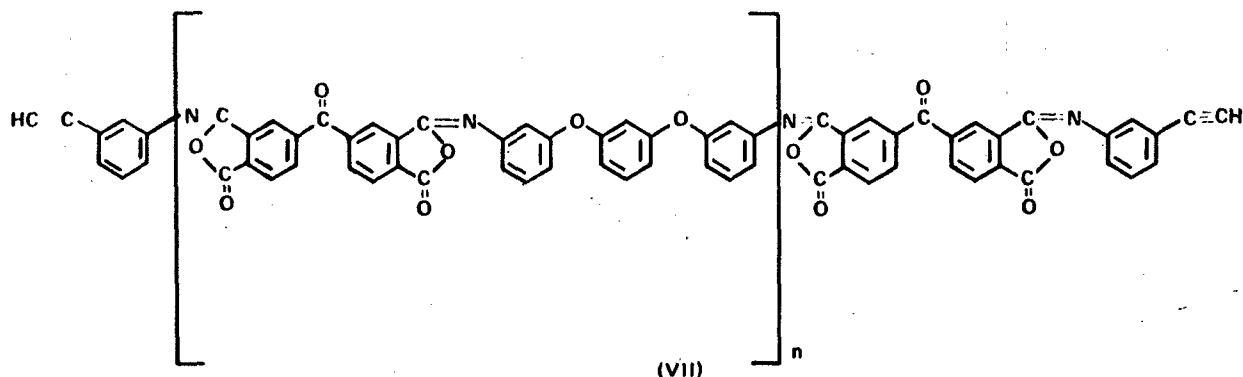


Figure 1. Imide-isoimide formation and conversion.

The extension of this approach to previously intractable polyimides was obvious, and the initial application was made to Thermid 600, whose isoimide form is shown in Structure VII.



This version of Thermid 600 was identified as HR60XP where X was the value of n except when $n=1$, then $X = 0$. In the other cases X equaled the value of n. The value n was also called the degree of polymerization of the oligomer. Among the cyclodehydrating reagents, only trifluoroacetic anhydride (TFAA) and N,N'-dicyclohexylcarbodiimide (DCC) converted amic acid precursor to the isoimide oligomer in high yield. The oligomer made by dehydration using TFAA was invariably contaminated with fluorine-containing impurities which could not be removed by the usual purification techniques. It was proposed that these impurities are formed by hydrolysis of the isoimide moiety by trifluoroacetic acid formed during the dehydration by TFAA (Reference 9). When DCC was used as a cyclodehydrating agent a relatively neutral by-product, N,N'-dicyclohexylurea, was formed. This by-product produced no undesirable side reactions and was easily removed. On the basis of this comparison, DCC was the preferred reagent to prepare these oligomers.

The HR60XP oligomers were characterized by high solubility in solvents such as cyclic ethers (tetrahydrofuran and dioxane), glymes, mixed solvent systems such as toluene and acetone and the usual amide type solvents (N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidinone). Also, the Tg of the uncured oligomer was appreciably lower (about 60°C) than the imide version. These factors helped to widen the processing window in that the lower Tg of the resin resulted in lower molding temperatures and an increase in gel time. With the introduction of isoimide structural units, previously intractable and insoluble acetylene-terminated polyimide oligomers were made processible. The isoimide was then thermally converted to the imide during the cure cycle resulting in a cured resin similar to that obtained by starting with the imide version.

This research program addressed two major tasks. The first task was to study the chemistry of the formation of isoimides from the monomers, APA, BTDA and APB to give HR600P, HR602P and HR605P. The techniques used to characterize these oligomers were explored and selected properties are presented. Detailed synthetic procedures are described in this report.

The second task extended this study to less expensive versions of acetylene-terminated isoimides, using the techniques generated in the first task.

2.0 RESULTS AND DISCUSSION

TASK I

Task I addressed the chemistry of the synthesis of HR60XP acetylene-terminated isoimide oligomer. The objective of this task was to develop a synthetic procedure for these oligomers and then to use the best procedure to synthesize representative samples of these oligomers to measure some selected properties, both before and after molding. The specific oligomers that were synthesized under this task were HR600P, HR602P and HR605P.

Determination of Isoimide, Imide and Amic Acid Ratios

The structure of the acetylene-terminated isoimide oligomer depicted by Structure VII is an idealized version of HR600P. The oligomer consisted primarily of isoimide with lesser quantities of imide and amic acid. As the optimization of the preparation of HR60XP oligomers required careful characterization and quantification of the constituents present, the ratio of isoimide to imide to amic acid from oligomers obtained by various synthetic procedures had to be compared. The HR60XP oligomers were prepared by first forming the amic acid precursor by the reaction of stoichiometric quantities of benzophenonetetracarboxylic dianhydride (BTDA), 1,3-bis(3-aminophenoxy)benzene (APB) and 3-aminophenylacetylene (APA). The amic acid precursor then underwent a cyclodehydration reaction with *N,N'*-dicyclohexylcarbodiimide (DCC) to form the isoimide. During the cyclodehydration process, the DCC was converted quantitatively to *N,N'*-dicyclohexylurea (DCU). The DCU was insoluble in the THF solvent and was separated by simple filtration from the THF-soluble HR60XP oligomer. The oligomer was then isolated by precipitation in a nonsolvent such as isopropyl alcohol or hexane. The relationship between the reaction conditions and the isoimide/imide/amic acid ratio was then evaluated.

A number of techniques have been described to determine these ratios. One method involved the differences in the absorption spectra of a set of very suitable model compounds, *N*-phenylphthalisoimide, *N*-phenylphthalimide, and phthalanilic acid. In this method the change in concentration of *N*-phenylphthalisoimide was followed by the absorbance at 330 μ , a wavelength where both *N*-phenylphthalimide and phthalanilic acid exhibit negligible

absorption (Reference 32). Infrared spectroscopy was also used to determine the ratios of isoimide to imide (References 15, 33, 34). In this method, the concentration of N-phenylphthalisoimide and N-phenylphthalimide in mixtures were determined using the absorption band at 920 cm^{-1} attributed to the isoimide and 1380 cm^{-1} band attributed to the imide (Reference 33). A 5 percent precision using infrared absorption bands was possible as compared to results from the more precise gas chromatographic method. Infrared spectroscopic analysis of a number of derivatives of phthalimides and of phthalisoimides (Reference 15) revealed that the infrared spectra of all phthalimides showed $\nu(\text{C}=\text{O})$ at $1789\text{--}1841\text{ cm}^{-1}$, $\nu(\text{C}=\text{N})$ at $1689\text{--}1727\text{ cm}^{-1}$ and a characteristic broad base band at $900\text{--}934\text{ cm}^{-1}$ which could be attributed to the lactone ring with an exocyclic double bond.

When using Fourier-transform infrared (FT-IR) spectroscopy to quantize isoimide/imide/amic acid concentration in acetylene-terminated isoimide oligomers, it was necessary to find spectral regions that could be assigned to each constituent where overlapping absorptions were absent. Even though FT-IR was capable of integrating areas under the various peaks, the problem of designating a proper base line to a peak varied from spectrum to spectrum and gave inconsistent results. Other problems were attributed to interfering peaks. For example, if the 1805 cm^{-1} peak, attributed to isoimide, was used and the area of the curve from 1900 to 1755 cm^{-1} was bracketed, the results were only valid for very low concentrations of imide because of the proximal presence of a peak at 1760 cm^{-1} , attributed to imide. Figures 2 and 3 depict FT-IR spectra on KBr samples of HR600P and Thermid MC600, which is the imide form. It was decided that the more meaningful method of quantizing the isoimide/imide/amic acid was to use the peak heights of 936 cm^{-1} for the isoimide, 1375 cm^{-1} for the imide, and 1540 cm^{-1} for the amic acid.

Figure 4 depicts the technique used to quantize the oligomers. The spectral peak at 1480 cm^{-1} is included only in that it appears in all the HR60XP oligomers. The absorbance mode was used because the concentration was proportional to the absorbance. A judgment had to be made regarding the baseline. This was done by using two well defined minima of adjacent peaks and connecting them with a straight line. The peak height ratios for isoimide/imide/amic acid were then $1.00/0.11/0.02$. Through the use of appropriate model compounds, absolute values for the concentration of these moieties could possibly be obtained. However, the technique described here can be effectively used to compare oligomers prepared by various methods.

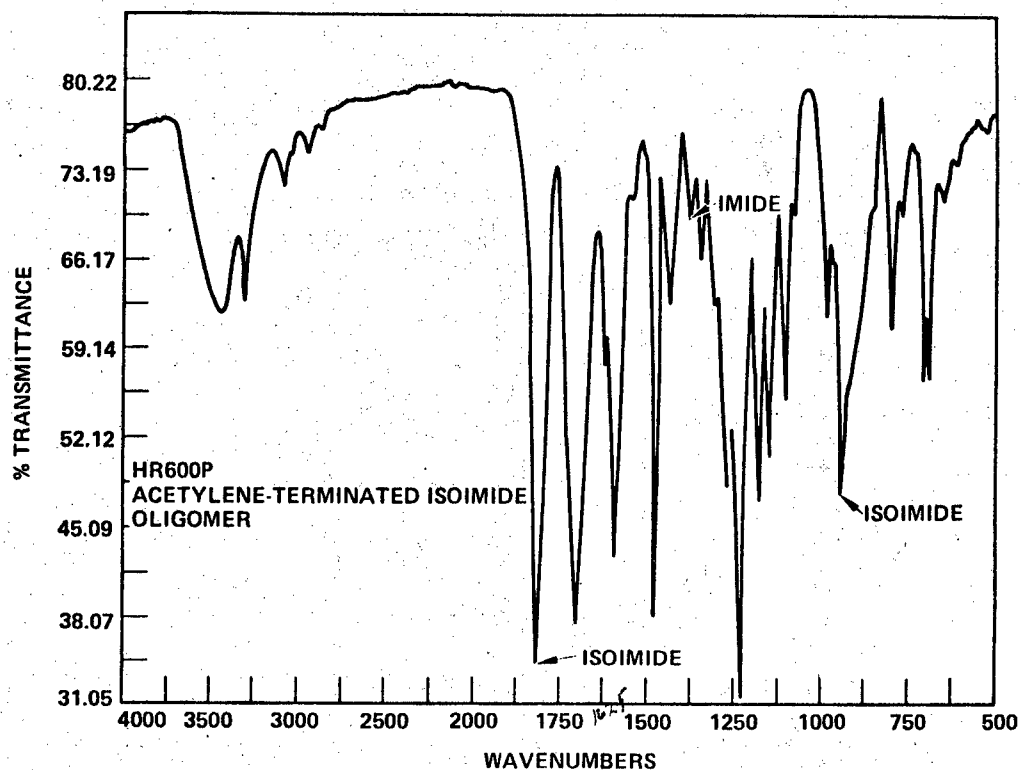


Figure 2. FT-IR spectrum of HR600P acetylene-terminated oligomer.

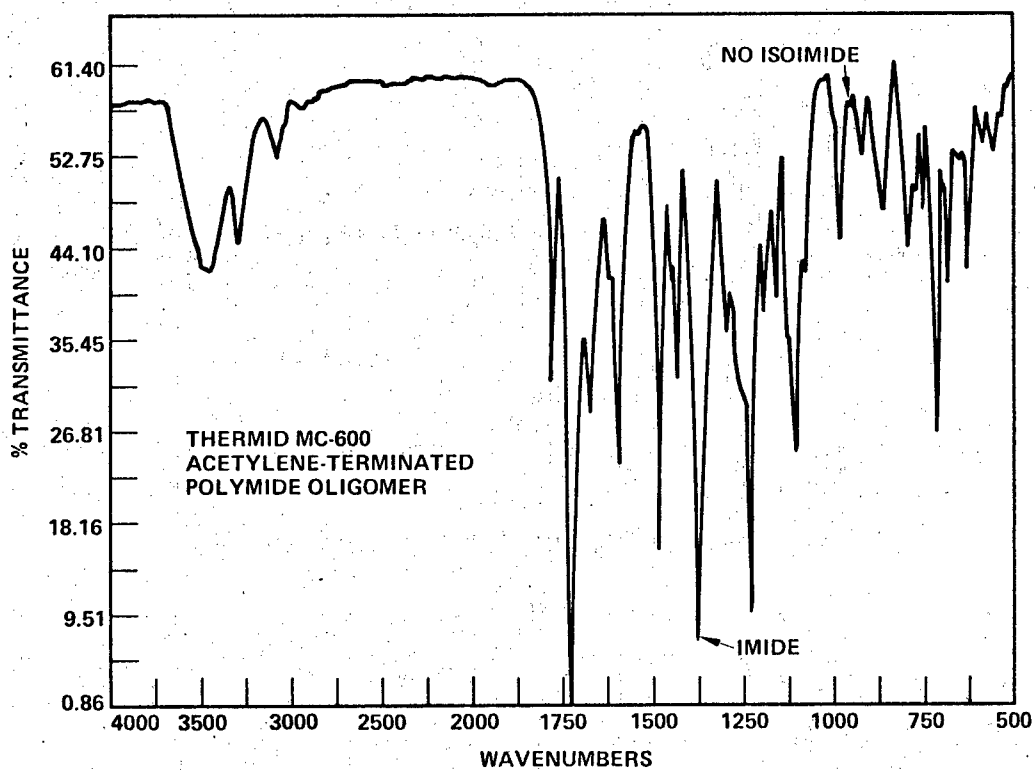


Figure 3. FT-IR spectrum of Thermid MC-600.

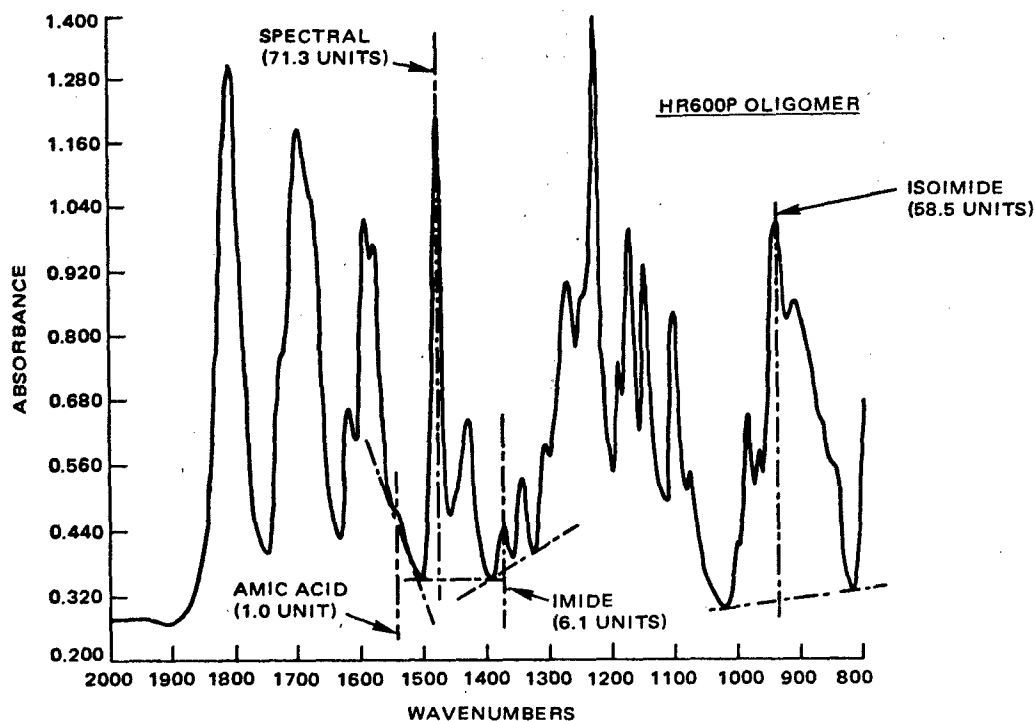


Figure 4. Quantizing the isoimide, imide and amic acid content of HR600P oligomer by FT-IR.

HR60XP Synthesis Study

The preparation of the HR60XP acetylene-terminated isoimide oligomers was aimed at a procedure that could be adapted to a pilot plant operation, yielding a product of high quality while minimizing the imide and amic acid, and residual volatiles. The study was initiated with the synthesis of the simplest member of HR60XP series, HR600P, where $n=1$ in Structure VII. Figure 5 shows the flow diagram for the oligomer preparation. Tetrahydrofuran and dioxane were evaluated as reaction solvents which could easily be removed from the product and be compatible with the nonsolvent in the final precipitation step. In the case of tetrahydrofuran, either hexane or isopropyl alcohol could be used as a precipitation solvent because of the mutual solubility of these solvents with each other, whereas for dioxane only isopropyl alcohol could be used because it is only partially miscible with hexane.

Tetrahydrofuran was chosen as the reaction solvent because of its purity, low cost, good solvent properties (both for the reactants and the oligomers), and low boiling and freezing points. The initial study was done with the concentrations of the reactants in the range of 7-24%. The first step of the synthesis was to form the amic acid precursor. In this preparation a

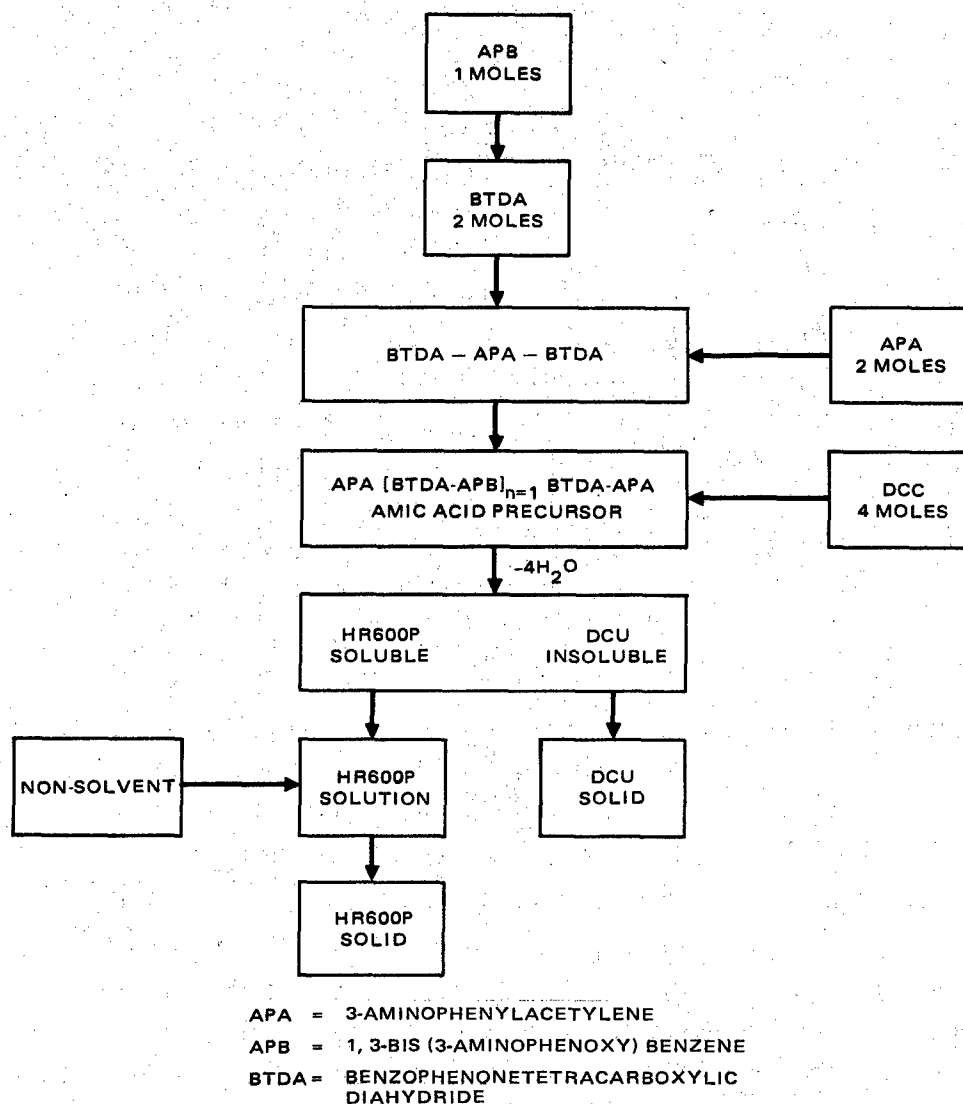


Figure 5. Flow diagram for the synthesis of HR600P oligomer.

small amount of imide formation took place because of cyclodehydration of amic acid. To determine the temperature sensitivity of the imide/amic acid ratio, amic acid precursors were prepared at ambient temperature and under refluxing THF (67°C). The following results, shown in Table 1, were obtained:

TABLE 1. EFFECT OF REACTION TEMPERATURE ON IMIDE/AMIC ACID RATIO DURING AMIC ACID SYNTHESIS

Temperature (°C)	Imide/Amic Acid Peak Height Ratio by FTIR
Room Temperature (M1126-10A)	0.04/1.00
67°C (K1543-138)	0.14/1.00

The results indicated that at the temperature of refluxing THF (67°C), more than three times the quantity of imide was formed than at ambient temperature.

Incomplete conversion of amic acid to the isoimide can yield an oligomer which upon cure would thermally cyclize to give off water. The volatile byproducts produced during cure would cause voids if not removed. An experiment was designed to learn if amic acid impurities could be selectively removed by aluminum oxide. An oligomer was synthesized which contained 5 percent free amic acid. This was accomplished by using only 95 percent of the DCC for the cyclodehydration step. A portion of the oligomer (M1139-16) in THF was treated with an equal weight of neutral aluminum oxide, Brockman Activity Grade 1. The solution was filtered and the oligomer isolated by precipitation in hexanes. The same process was repeated using basic aluminum oxides. The results are shown in Table 2.

TABLE 2. AMIC ACID SCAVENGING BY ALUMINUM OXIDE

Oligomer Treatment	Imide/Isoimide/Amic Acid FT-IR Relative Peak Heights
Untreated Oligomer (M1139-16)	0.106/1.000/0.0981
Neutral Aluminum Oxide Treatment (M1139-19)	0.124/1.000/0.241
Basic Aluminum Oxide Treatment (M1139-20)	0.115/1.000/0.0170

Several experiments were performed relating the stoichiometry of the DCC to the amount of amic acid present in the final product. The solids content were kept in the range of 10-15 percent. Thus, one experiment (M1126-1) used a 1 percent excess of DCC and the other (M1126-3) used a 5 percent excess. The reactions were carried out at room temperature. The oligomers were washed with isopropyl alcohol to remove any residual DCC or DCU and then vacuum dried at 85°C. In both cases, only trace amounts of amic acid were found. In fact, the amounts were about the same (based on the 1540 cm^{-1} absorption peak in the infrared spectrum) as found in the fully imidized oligomer (Thermid MC 600). The isoimide/imide FT-IR absorbance ratio for both samples, M1126-1 and M1126-3 was 1.00/0.17.

Although the use of hexane results in a nearly quantitative precipitation of the oligomer from the reaction mixture, the product had a high volatile content because of entrapped solvents and other impurities. Polyisoimides have been known to react with alcohols to form polyamide-esters (Reference 35). Although this may be true for high molecular weight polyisoimides, it was not so in the case of the acetylene-terminated isoimide oligomers described here. Thus, in the workup of the HR600P oligomer identified by M1126-27, precipitation by isopropyl alcohol gave FT-IR relative absorption peak heights for isoimide/imide/amic acid of 1.00/0.28/0.09. Isopropyl alcohol is preferred as a precipitation solvent in

that it solubilizes low molecular weight byproducts such as DCU and also tends to precipitate out the oligomer as a fine powder rather than as a granular mass when hexane is used. Also, as the degree of polymerization of the oligomer increases, the clean-up of the oligomer is more difficult particularly if hexane is used as a precipitating solvent. Table 3 illustrates the effect of different precipitating solvents on the synthesis of HR600P, HR602P and HR605P oligomers.

TABLE 3. EFFECT OF PRECIPITATING SOLVENT ON VOLATILE CONTENT AND COMPOSITION OF HR60XP OLIGOMERS

Oligomer	Experiment Number	Prec. Solv.	Softening Pt.	Percent Volatiles*	FT-IR Rel. Pk. Hts Isoimide/Imide/Amic Acid		
HR600P	M1126-29A	Hexane	158°C	3.0	1.00	0.16	0.04
	M1126-29B	1PA	165°C	2.1	1.00	0.17	0.06
HR602P	M1126-31A	Hexane	170°C	6.3	1.00	0.10	0.04
	M1126-31B	1PA	170°C	3.1	1.00	0.08	0.02
HR605P	M1126-33B	Hexane	182°C	3.0	1.00	0.05	0.02
	M1126-33A	1PA	177°C	3.8	1.00	0.04	0.05

*The percent volatiles obtained by heating a sample at 250°C for 30 minutes.

The use of isopropyl alcohol as a precipitating solvent did not seem to form a polyamide-ester as seen in Table 3. Also, there appeared to be a trend in the lower volatile content, especially for HR600P and HR602P. In the case of HR605P, the percent volatiles content is not significantly different when the two precipitating solvents are compared.

There is evidence based on FT-IR results that the cyclodehydration step by the DCC is very rapid, even at low temperatures. Aliquot samples of oligomer taken one hour after the addition of the DCC showed that almost all the amic acid precursor had been converted to the isoimide. The high solubility of the oligomer in THF demonstrated in M1126-29 that an oligomer could be prepared using concentrations of high solids. The relative peak heights for isoimide/imide/amic acid were comparable to those obtained for lower concentrations of reactants. The reproducibility of these reaction conditions was demonstrated in the preparation of a one kilogram batch of HR600P in experiment M1126-39D. The product had a relatively low volatile content of 1.27 percent and isoimide/imide/amic acid relative absorbance peaks of 1.00/0.07/0.07 respectively.

Gel permeation chromatography for this oligomer showed a $M_w = 4036$ and an $M_n = 1169$. The plot of molecular weight versus percent of polymer composition is shown in Figure 6.

About 35 percent of the oligomer was the diisoimide of BTDA and APA, a value consistent with an earlier study done by Gulf Oil Chemicals using statistical analysis. In this case, the expected value would have been 25 percent. The higher value obtained here is due to the fact

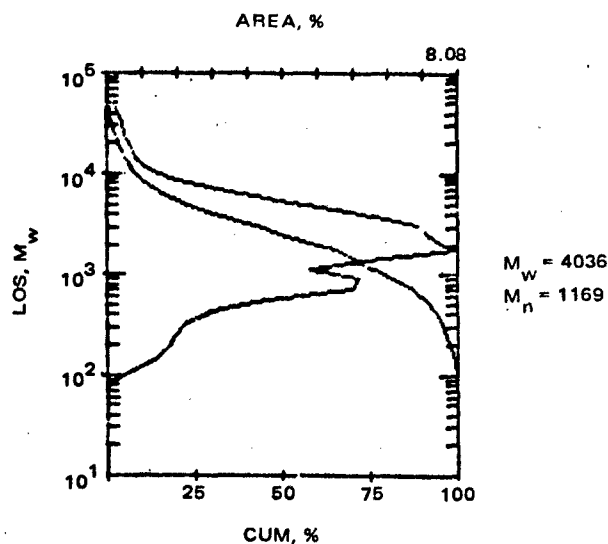


Figure 6. Gel permeation chromatogram of HR600P, Lot M1126-39D.

that a slurry of BTDA in THF was used rather than a homogeneous solution. Thus, the concentration of BTDA was higher towards the latter part of the addition of the APB resulting in a higher percentage of the reaction mixture being the diisoimide of BTDA and APA.

Under a separate program, a 100 pound pilot plant batch of HR600P was prepared by Cyclo Chemical Co., Los Angeles, CA. In this batch, the M_w was found to be 2634 and the M_n to be 1066 (Figure 7). The range was even more narrow in this case. Again, this could be explained by the heterogeneous nature of the addition of the APB to the slurry of BTDA in the THF. Isoimide/imide/amic acid ratio as found from FT-IR was comparable to that for lot M1126-39D.

The rheological behavior of HR600P (Lot M1126-39D) was studied using a rheometric dynamic spectrometer. The material was applied as a powder between two parallel plates. Measurements were made at 190°C and 210°C (Figures 8 and 9). At 190°C, the minimum approximate viscosity was 20,000 poise with a gel time of 15-16 minutes. At 210°C, the minimum viscosity was 1600 poise with a gel time of 5-1/4 minutes. It was not possible to obtain similar temperature measurements for Thermid MC-600 because of its very high melting point (>210°C). However, at 250°C, (Figure 10), the viscosity was 10,000 poise and the gel time one minute.

Differential scanning calorimetry (DSC) for a representative sample of HR600P (Lot M1126-1) is shown in Figure 11. The maxima occurs at 243°C using a heating rate of 10°C/minute in nitrogen. Figure 12 depicts a comparison of the DSC for an HR600P oligomer and the isomeric acetylene-terminated polyimide, Thermid 600. It is significant that the base was much broader for the isoimide form, although the maxima occurred approximately at the same temperature. The onset of homopolymerization roughly corresponded to the beginning of melting of the oligomers and was one of the reasons for the broader base in the case of HR600P because of the lower melting point.

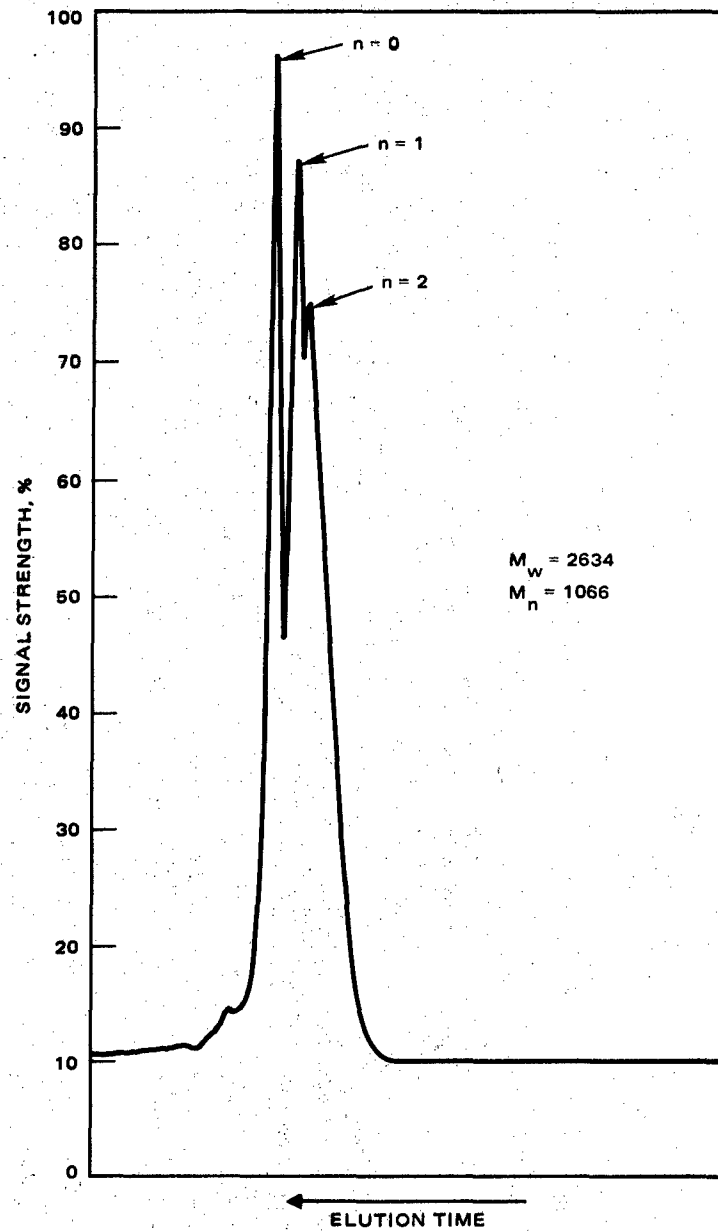


Figure 7. Gel permeation chromatogram of a pilot plant run of HR6OOP oligomer (Batch O1-2018).

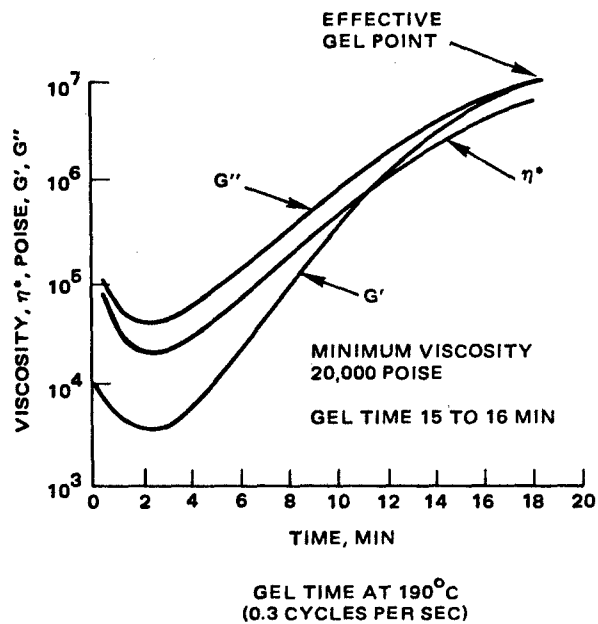


Figure 8. Rheometric behavior of HR600P (Lot M1126-39D) at 190°C.

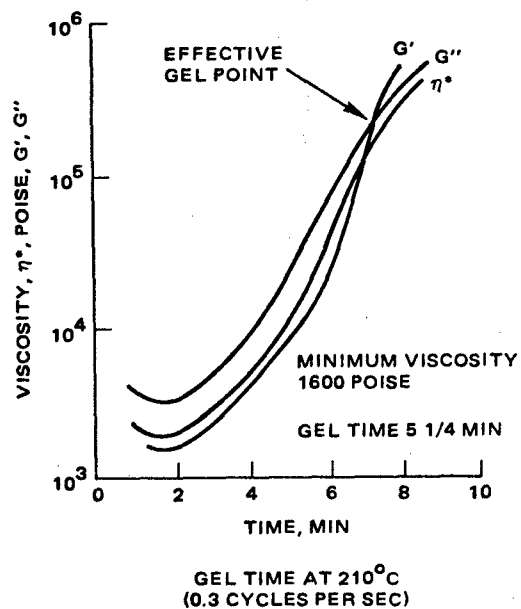


Figure 9. Rheometric behavior of HR600P (Lot M1126-39D) at 210°C.

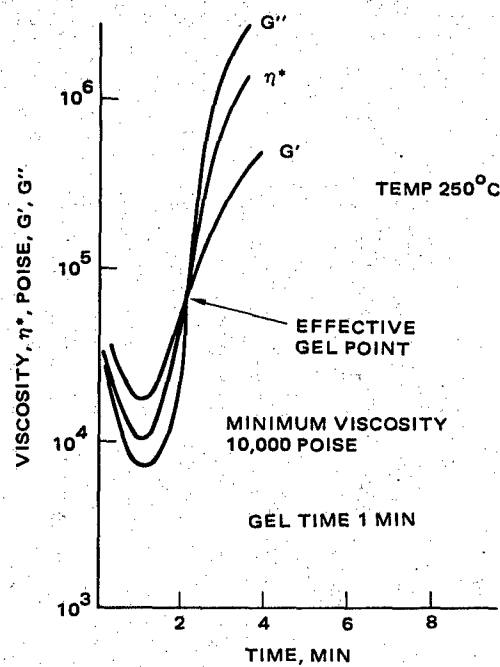


Figure 10. Rheometric behavior of Thermid MC-600 at 250°C.

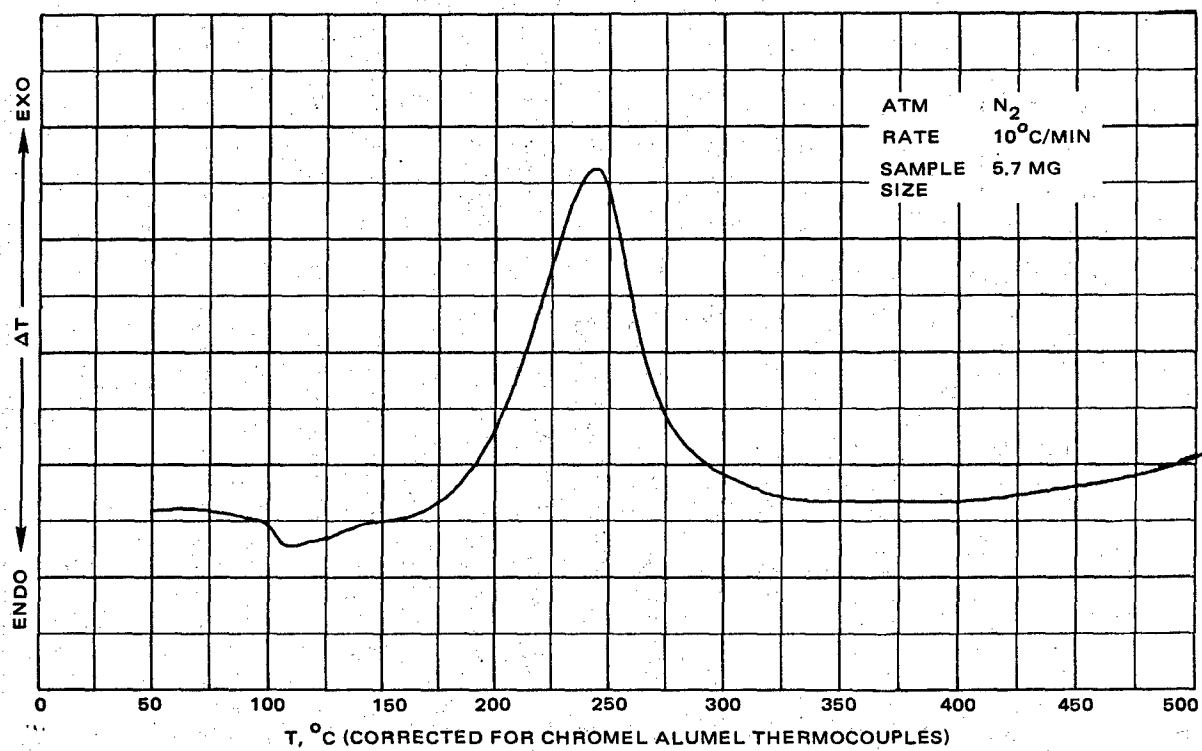


Figure 11. Differential scanning calorimetry (DSC) for HR600P (Lot M1126-1).

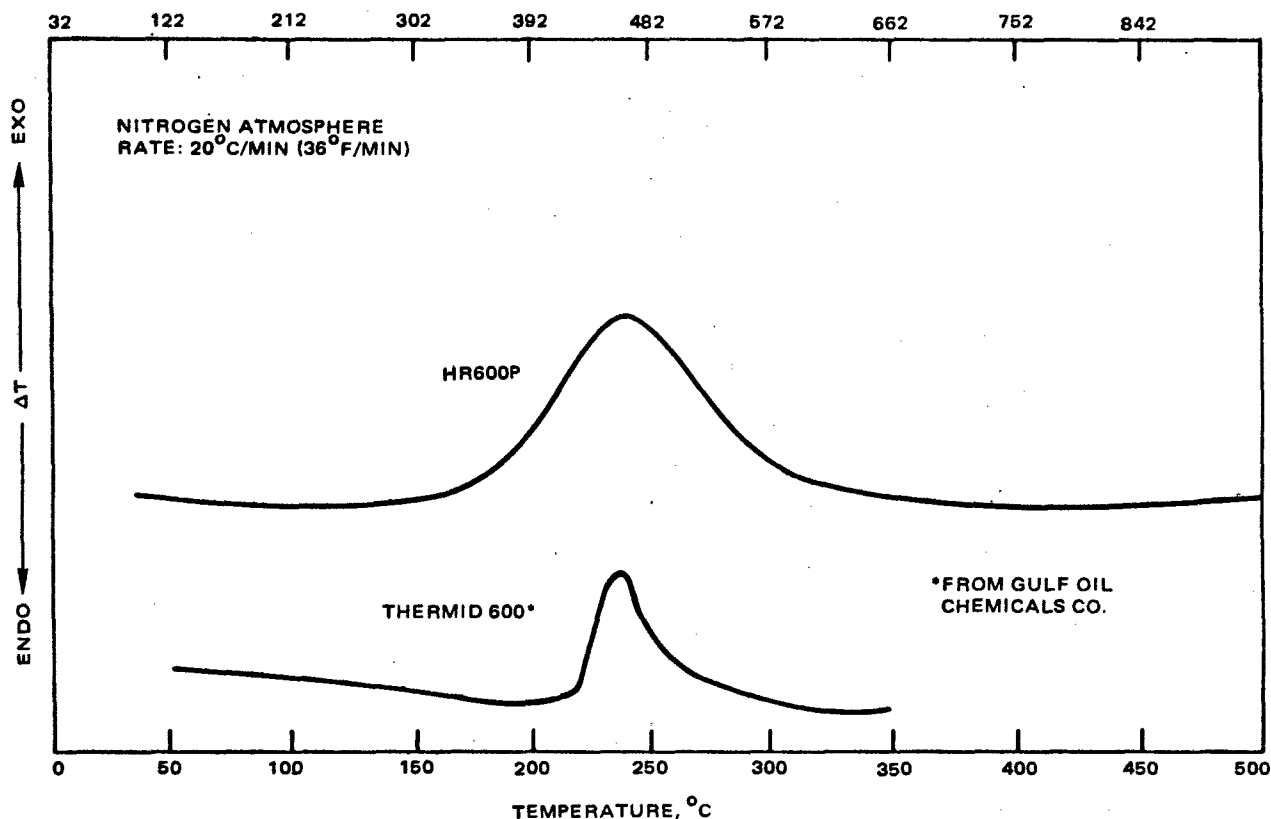


Figure 12. Differential scanning calorimetry (DSC) curves for thermid 600 and HR600P resins.

The higher homologues of HR600P, namely HR602P and HR605P were prepared using the method worked out for HR600P. A 250 gram batch of HR602P (experiment M1126-42) as well as a number of other batches of this oligomer were prepared. These oligomers melted at approximately 170°C and were very soluble in tetrahydrofuran. Gel permeation chromatography of a sample of HR602P (experiment M1126-31B) showed a M_w equal to 4597 and a M_n equal to 1717. The chromatogram is depicted in Figure 13.

In a similar manner, a number of batches of HR605P oligomer was prepared. A typical batch had a M_w equal to 10,019 and a M_n equal to 2067. A gel permeation chromatogram is depicted in Figure 14 for experiment M1126-33A. This oligomer had a melting point of 177°C.

DSC curves for HR602P and HR605P are depicted in Figures 15 and 16. The maxima for HR602P (Lot M1126-42) was 257°C and for HR605P (Lot M1126-48) was 262°C. Here again, like that for the HR600P, the onset of the exotherm corresponded to the melting of the oligomer.

The FT-IR spectra for HR600P, HR602P and HR605P, all made by the same procedure are depicted in Figures 17, 18 and 19. The following values were obtained for the absorbance spectra ratio for isoimide/imide/amic acid and are shown in Table 4.

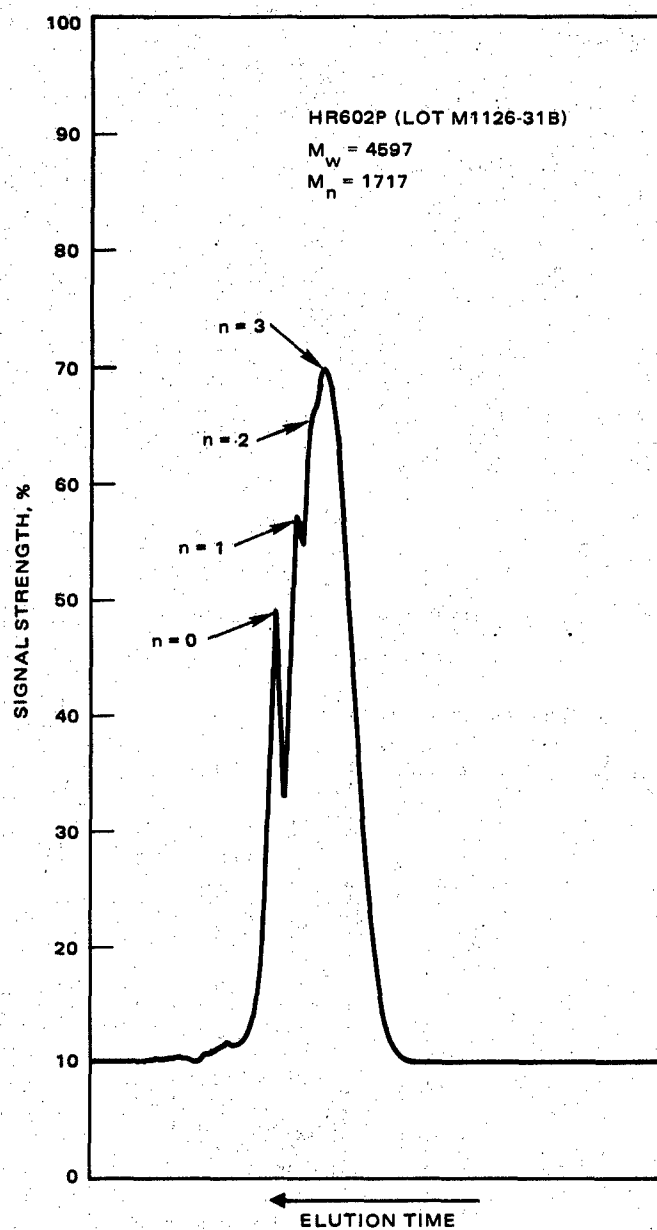


Figure 13. Gel permeation chromatogram of HR602P oligomer (Lot M1126-31B).

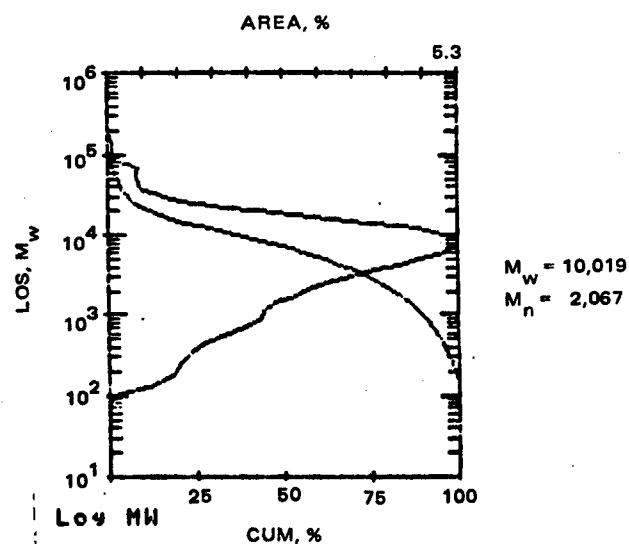


Figure 14. Gel permeation chromatogram for HR605P (Lot M1126-33A).

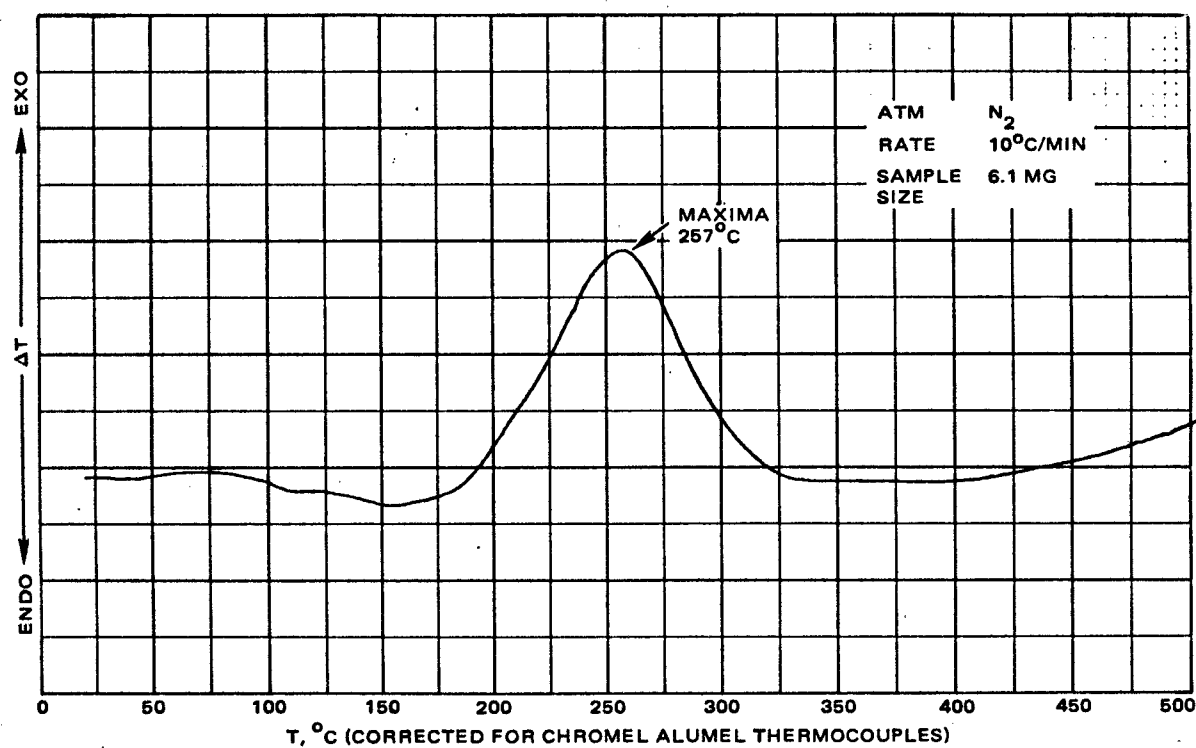


Figure 15. Differential scanning calorimetry (DSC) for HR602P oligomer (M1126-42).

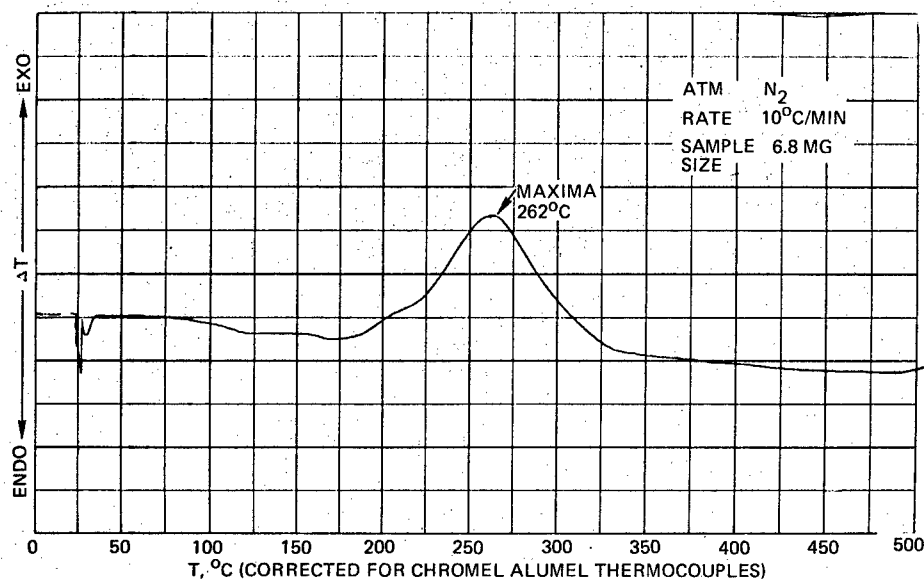


Figure 16. Differential scanning calorimetry (DSC) curve for HR6O5P oligomer (M1126-48).

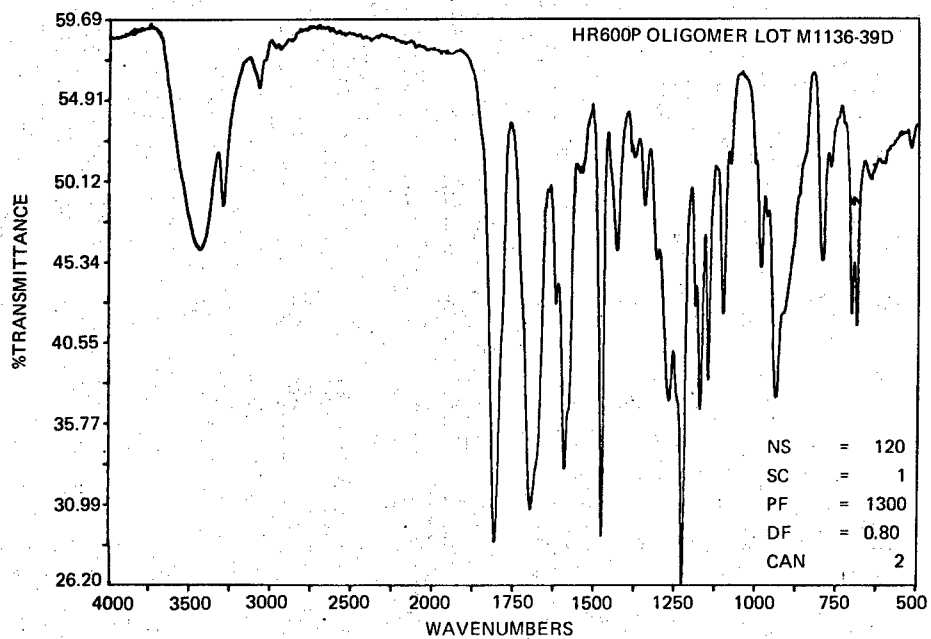


Figure 17. FT-IR spectra of HR6OOP oligomer, Lot Number M1126-39D.

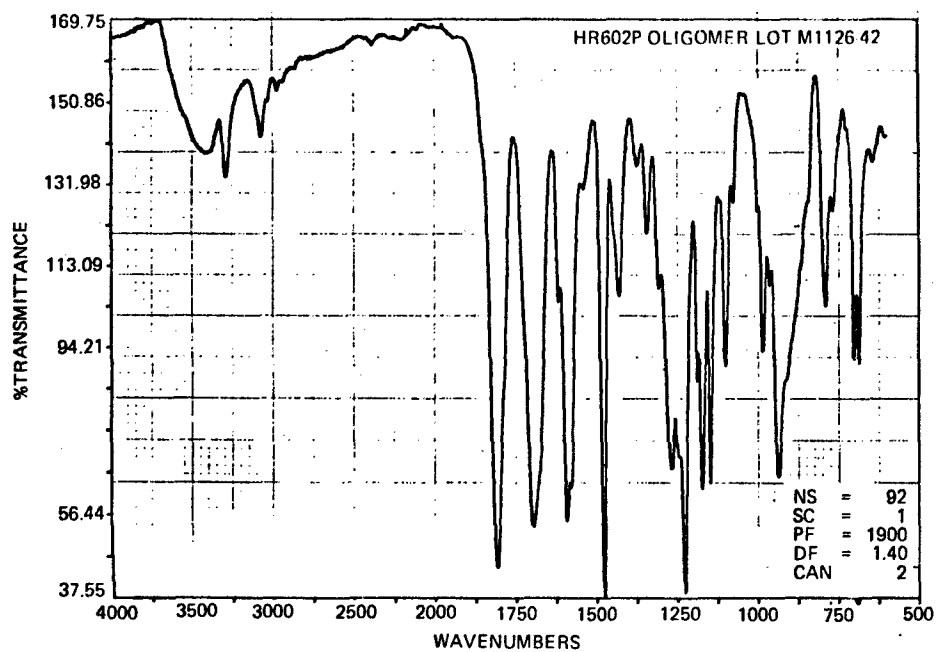


Figure 18. FT-IR spectra of HR602P oligomer, Lot Number M1126-42.

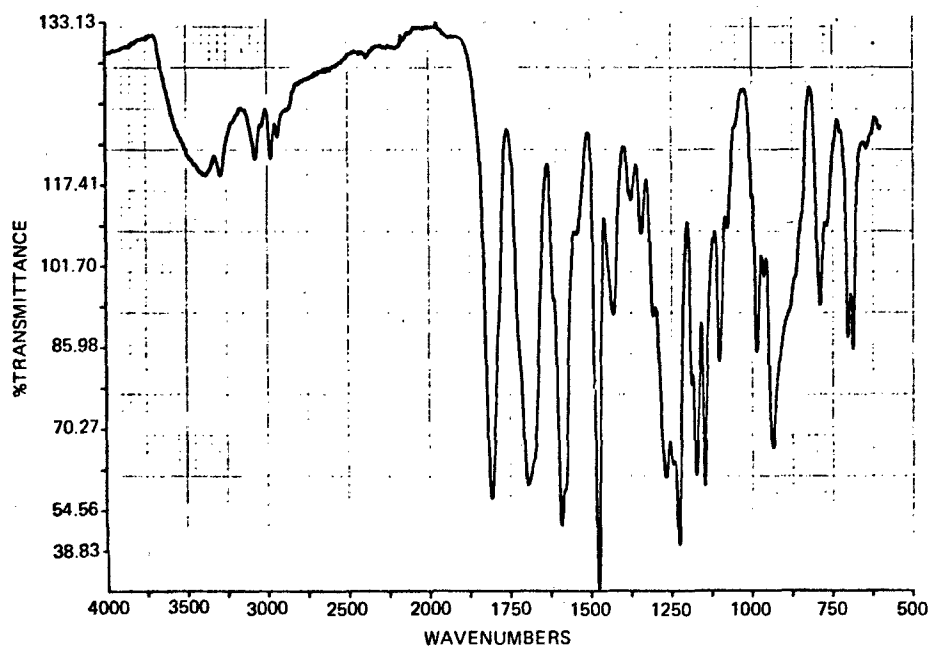


Figure 19. FT-IR spectra of HR605P oligomer, Lot M1126-44.

TABLE 4. FT-IR RELATIVE PEAK HEIGHTS FOR HR60XP OLIGOMERS

Oligomer HR60XP	Experiment Number	FT-IR Relative Absorbance Peak Heights		
		Isoimide	Imide	Amic Acid
HR600P	M1126-39D	1.00	0.07	0.07
HR602P	M1126-42	1.00	0.06	0.04
HR605P	M1126-44	1.00	0.10	0.05

HR60XP Cure Study

Two reactions took place when curing an acetylene-terminated isoimide oligomer. These reactions were the isomerization of the isoimide to the imide and the homopolymerization of the acetylene. There have been a number of studies addressing the thermal isomerization. One study compared the rate for a model compound, N-phenylphthalisoimide and that of a polymer, polypyromellitisoimide (Reference 33). The results of this study are depicted in Figure 20. The plot showed that the total conversion of the isoimide to the imide occurred much faster for the relatively low molecular weight model compound than for the polymers. Although conversion was complete a higher temperature was required for the polymer. This result can be attributed to the higher mobility of the model compound; isomerization occurred in the liquid phase (m.p. 116°C) while the conversion of the polypyromellitisoimide proceeded in the solid state. In the case of the model compounds, it was not possible to detect the isoimide by the use of gas chromatography, a much more sensitive method than infrared spectroscopy. This indicated that the conversion was quantitative. Similarly, a comparison of the infrared spectra of molded and cured (700°F/16 hours in air) of Thermid MC-600 and HR600P appeared to be identical (Figure 21). Figure 22 depicts the infrared spectra of chemical changes resulting in a HR600P (Lot M1126-39D) oligomer as a result of heating at 450°F (232°C) for 2-1/2 minutes. The conversion to the imide was fairly rapid. Even after 2-1/2 minutes a large decrease in the absorbance at 940 cm^{-1} (attributed to the isoimide) and a large increase in absorbance at 1375 cm^{-1} attributed to the imide) could be seen. The acetylene absorbance at 3290 cm^{-1} decreased only slightly showing that the homopolymerization was a slower process at this temperature. Figure 23 followed the same change two hours later. The isoimide structure and the acetylenic structure were no longer apparent from the infrared spectra.

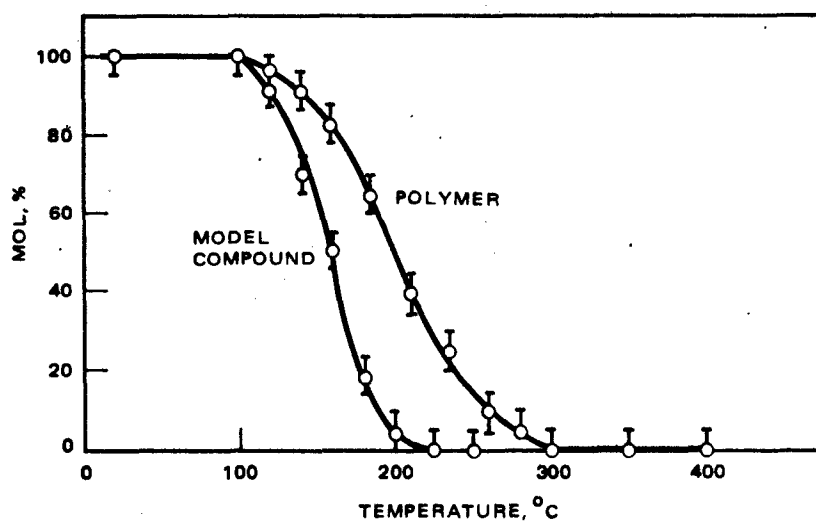


Figure 20. Conversion of n-phenylphthalisoimide into n-phenylphthalimide and polypyromellitisoimide into polypyromellitimide as a function of temperature (samples heated for 15 min.) (Reference 3).

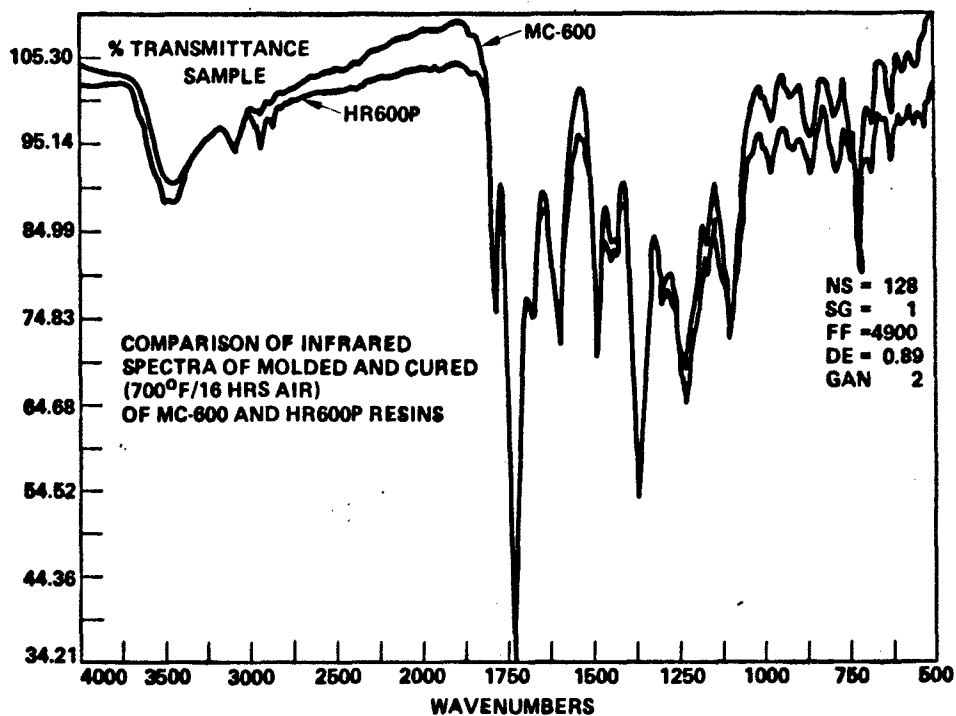


Figure 21. Comparison of infrared spectra of molded and cured (700°F/16 hours) of thermid MC-600 and HR600P resins.

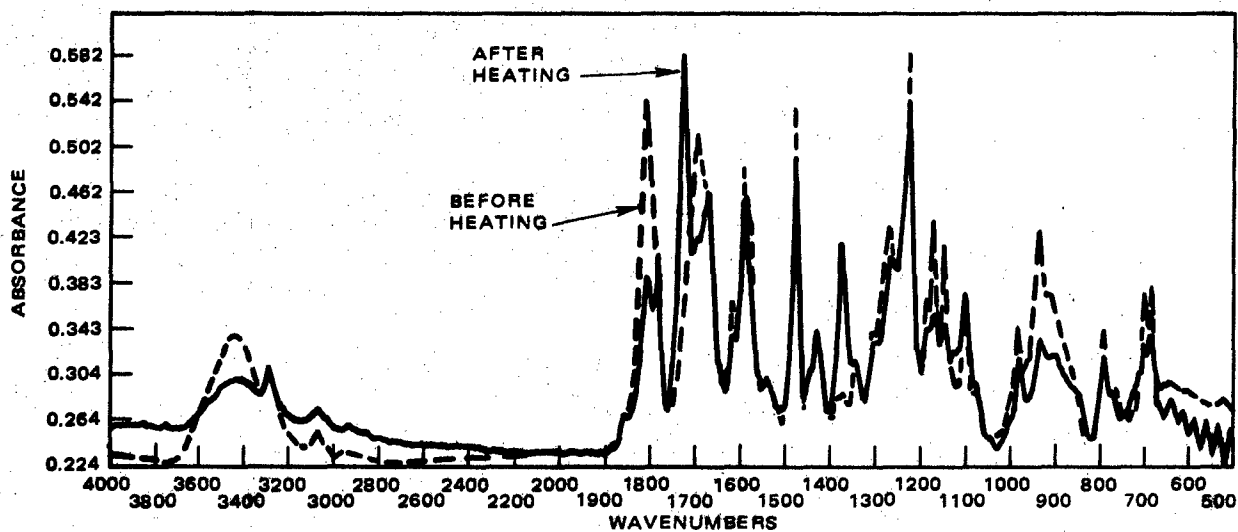


Figure 22. FT-IR depicting chemical changes in HR600P oligomer (Lot M1126-39D), as a consequence of heating at 450°F (232°C) for 2-1/2 minutes.

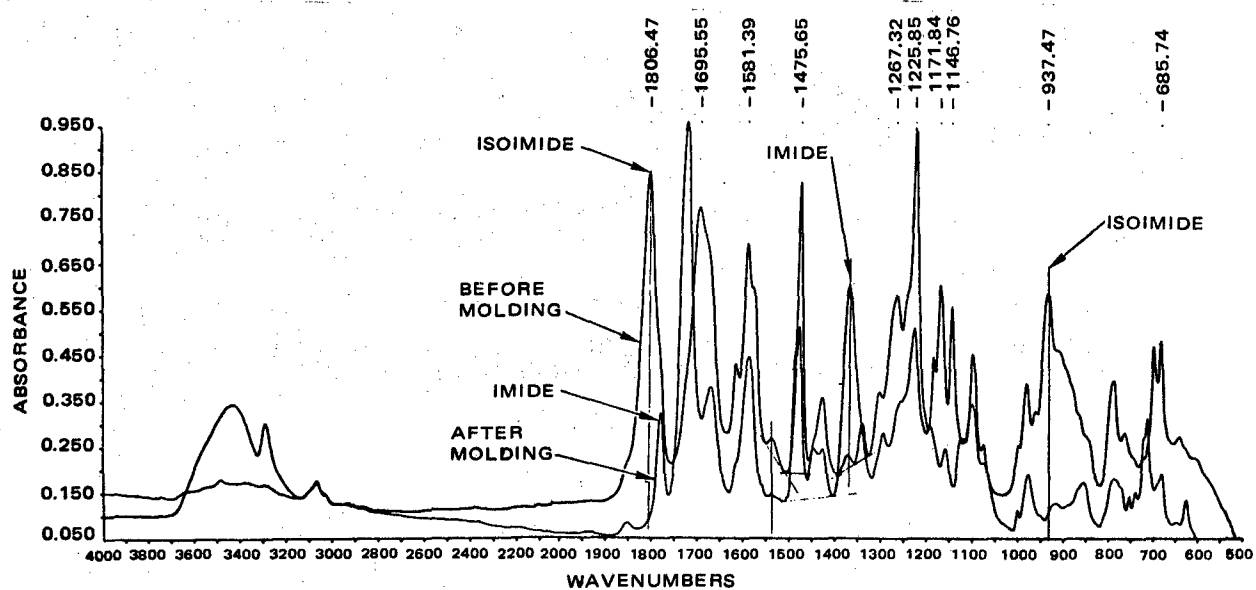


Figure 23. FT-IR depicting chemical changes resulting in HR600P oligomer as a consequence of compression molding at 450°F (232°C) 2 hr. (Lot No. M1226-39D).

A study of the effect of cure conditions on the glass transition temperature of neat molding of HR600P oligomer (Lot M1126-39D) was performed. Before molding, the resin was advanced at 450°F (232°C) for 2-1/2 minutes. It was then molded at this temperature and kept in the mold at temperature for 1 hour. The oligomer was then removed from the mold and postcured using the following heat cycle:

RT → 400°F within 4 hours

Hold 2 hours at 400°F

400°F → 600°F within 4 hours

Hold 2 hours at 600°F

600°F → 700°F within 2 hours

Hold for a specified number of hours at 700°F

The effect of the postcure on the Tg of HR600P is shown in Table 5.

TABLE 5. EFFECT OF POSTCURE ON Tg OF HR600P RESINS

HR600P Oligomer	Tg						Tg°C			
	700°F (Air)			700°F (Argon)			750°F (Air)		750°F (Argon)	
	4 Hrs	8 Hrs	15 Hrs	4 Hrs	8 Hrs	15 Hrs	4 Hrs	8 Hrs	4 Hrs	8 Hrs
Lot M1126-39D	304	306	338	—	—	350	306	350	—	332
Pilot Plant Run (Cyclo Chemical Co.) 1st Crop	—	300	350	—	311	350	325	354	—	358

Thermomechanical data was obtained on neat specimens made from M1126-39D which were postcured for only 4 hours in air at 700°F to give a Tg = 304°C. The thermomechanical properties are shown in Table 6. The remainder of the specimens were postcured in argon at 700°F (371°C) for 15 hours and found to have a Tg of 350°C.

TABLE 6. THERMOMECHANICAL PROPERTIES OF HR600P OLIGOMER (M1162-39D)*

Test Temperature °F (°C)	Tensile Strength psi × 10 ³	Flexural Strength psi × 10 ³	Elastic Modulus psi × 10 ⁶	Elongation Percent
Ambient	9.67	15.3	0.66	1.37
500°F (280°C)	—	7.8	0.28	—
550°F (288°C)	—	6.4	0.14	—
600°F (316°C)	2.18	—	0.16	3.8

*Postcured 4 hours at 700°F (371°C). Tg = 304°C.

Table 7 shows the effect of postcure time (700°F, Argon) on the thermomechanical properties of neat HR600P molded specimens.

TABLE 7. EFFECT OF POSTCURE TIME (700°F, ARGON) ON THERMOMECHANICAL PROPERTIES OF NEAT HP600P MOLDED SPECIMENS

Material/Postcure	Tensile Strength, psi × 10 ³		Elastic Modulus psi × 10 ⁶		Elongation, percent		T _g , °C
	Ambient	600°F (316°C)	Ambient	600°F (316°C)	Ambient	600°F (316°C)	
Lot M1126-39D							
Postcured 4 hrs/700°F	9.7	2.7	0.65	0.18	1.4	4.2	306
	9.8	1.9	0.64	0.16	1.2	3.0	
	9.5	1.9	0.68	0.15	1.5	4.2	
	<u>9.7 Ave</u>	<u>2.2 Ave</u>	<u>0.66 Ave</u>	<u>0.16 Ave</u>	<u>1.4 Ave</u>	<u>3.8 Ave</u>	
Postcured 15 hrs/700°F	8.0*	3.9	0.67	0.20	1.3	4.0	350
	8.7	4.2	0.70	0.20	1.4	4.0	
	<u>8.4 Ave</u>	<u>4.1 Ave</u>	<u>0.69 Ave</u>	<u>0.20 Ave</u>	<u>1.4 Ave</u>	<u>4.0 Ave</u>	
Large Pilot Plant Run Lot 01-2018							
Postcured 15 hrs/700°F	8.8	3.6	0.75	0.16	1.3	4.0	350
	8.4	4.5	0.72	0.20	1.2	4.5	
	8.4	—	0.71	—	1.2	—	
	<u>8.5 Ave</u>	<u>4.1 Ave</u>	<u>0.73 Ave</u>	<u>0.18 Ave</u>	<u>1.2 Ave</u>	<u>4.3 Ave</u>	

*Small break noted in break.

Specimens molded at 450°F for 1 hour at 4000 psi, postcured RT to 400°F in 2 hours; 400°F for 4 hours; 400°F to 600°F in 2 hours; 600°F for 4 hours and 700°F in argon for time indicated.

A postcure of approximately 15 hours at 371°C (700°F) was required to obtain a glass transition temperature at 350°C (662°F) on the neat resin. The longer postcure gave improved retention of 316°C (600°F) properties with only a minimal change in ambient properties. Also, the thermomechanical properties for the products of the pilot plant run and the laboratory batch were noted to be essentially the same.

Using a similar molding procedure as for the HR600P oligomer (Lot M1126-42), neat specimens of HR602P gave a T_g of 253°C (487°F) after postcuring for 16 hours at 371°C (700°F) in air. The lower glass transition temperature of the HR602P compared to the HR600P was not unexpected because of the lower crosslink density. The gel times (as determined by the wooden stick string method) were:

191°C (375°F)	5 minutes - 45 seconds
218°C (425°F)	4 minutes - 0 seconds

The melting point of the neat resin with a volatile content of 3.2 percent was 181°C which was only 20°C higher than the HR600P. The 700°F (371°C) postcure of molded samples of HR602P and HR605P made these samples unsuitable for good tensile strength measurements because the 700°F air postcure introduced surface changes which caused premature failure of

the sample under tension. A more realistic temperature would be a 600°F (317°C) temperature cure. Thus, tensile test specimens of HR602P (Lot M1126-68) and HR605P (Lot M1126-66) were prepared by compression molding the powder at 525°F (274°C) for 1 hour and 1000 psi. The specimens were subsequently postcured at 600°F (316°C) for 16 hours in an air circulating oven. Tg values of 262°C (504°F) were obtained for HR602P, and 248°C (478°F) for HR605P respectively. The best tensile strength for HR602P was 14,200 psi with a modulus of 570,000 psi. For HR605P, the best value was 7800 psi with an elongation of 1.46 percent and an elastic modulus of 590,000 psi. The unexpectedly low value for this specimen was possibly due to a surface defect. Values of about 15,000 psi for the tensile strength would be expected for the HR605P molded resin with at least 3-4 percent elongation. The technique used to measure tensile strength is too much dependent on the sample quality, whereas this is not the case for the measurement of the modulus. Thus, the values reported here for tensile strength represent minimum values only for neat resin moldings.

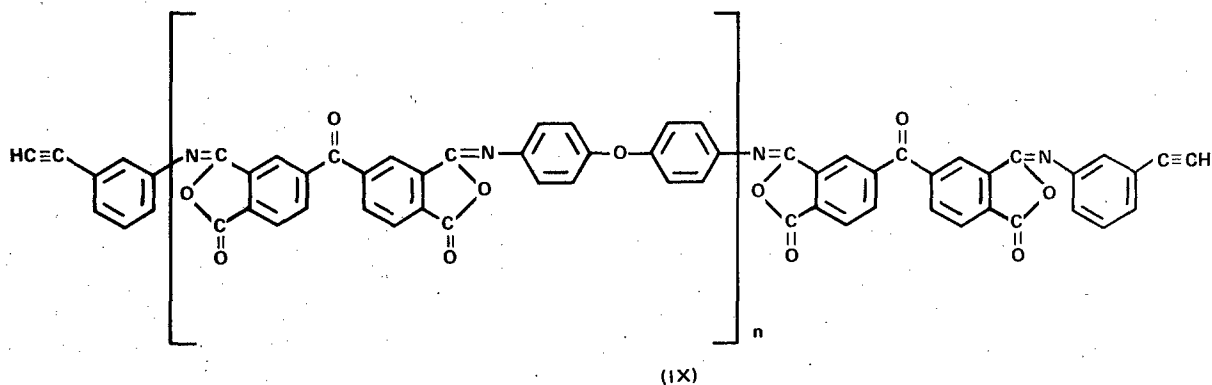
TASK II

Acetylene-Terminated Oligomers Based On Less Expensive Monomers

The imide structure when introduced into a polymer backbone generally yielded polymers which were characterized by high melting points and very low solubility, even for low molecular weight oligomers. This was one of the major problems to overcome when developing a processible acetylene-terminated polyimide. Special structural features had to be incorporated into the polymer backbone to introduce solubility and tractability. Only a few aryl-carboxylic dianhydrides are commercially available. Of these, benzophenonetetracarboxylic dianhydride (BTDA) was most applicable because the carbonyl group joining the two phthalic anhydride structures introduced flexibility into the polymer molecule.

The other dianhydride available, namely pyromellitic dianhydride, resulted in a very rigid structure. In the case of the aryl diamines available, the choice was also restricted. They either had aliphatic linkages which reduced the oxidative stability or were para oriented such as 4,4'-oxydianiline (ODA) which also introduced intractability into the molecule. Thus, to develop a tractable and processible prepolymer acetylene-terminated polyimide, it was necessary to develop an aryldiamine which had the structural features to give processability without compromising thermostability. The aryldiamine finally synthesized was 1,3-bis(3-aminophenoxy)benzene (APB). This monomer is very expensive to prepare, as is the capping agent, 3-aminophenylacetylene, and there are no good commercially available candidates to substitute. With the discovery that the isoimide structure introduced tractability and processibility into acetylene-terminated oligomers, and that the isoimide thermally and irreversibly converted to the imide, some of the expensive co-monomers used to prepare Thermid 600 type oligomers were replaced with commercially available compounds. Also,

further reduction in cost could be effected by reducing the quantity of the expensive 3-aminophenylacetylene, by increasing the degree of polymerization of the oligomer. The low cost monomer 4,4'-oxydianiline (ODA) was substituted for APB in the preparation of acetylene-terminated isoimide oligomers. To differentiate these oligomers from those made with APB, the oligomers made with ODA are referred to as HR60XP-Mod A oligomers. This oligomer is shown by Structure IX.



It was possible to use the same procedure to make HR600P-Mod A as for the previous oligomers made with APB. However, THF was a poorer solvent for the higher DP amic acid precursors and a gummy phase appeared in the reaction flask. For degrees of polymerization greater than one, i.e., where $n > 1$ in Structure IX, N,N'-dimethylacetamide (DMAC) could be used as a reaction solvent. With this solvent, it was possible to prepare HR602P-Mod A and HR603P-Mod A. The HR605P-Mod A could also be prepared in this solvent but it underwent reversion to the insoluble imide form in a relatively short time so that a rapid workup procedure had to be developed. Most likely the neat solid resin would be stable. The DMAC had the disadvantage of being a high-boiling solvent and tended to be retained by the oligomer. By careful washing and drying, it may be possible to reduce the volatile content of the oligomers to acceptable levels. The properties of the most representative HR60XP oligomers are presented in Table 8. As the degree of polymerization (DP) is increased, the melting point is raised. It was noteworthy that even with a DP of three the oligomer had a melting point equal to that of Thermid MC-600. The isoimide/imide ratio showed an increase as the DP is increased. This was not noted in the case of the HR60XP oligomers. This was consistent with the observation that HR605P isomerizes to the imide on standing in DMAC. Most impressive about modification A was the high Tg of the cured resins. In the past it was not possible to obtain high Tg for both the HR600P oligomer and the isomeric imide form without high temperature postcures (700°F(371°C)). Thus, with HR600P-Mod A and a 600°F (317°C) postcure an oligomer with a Tg of 370°C was obtained. Even the higher DP's of this modification showed relatively high Tg. Figures 24-27 depict the FT-IR spectra of the DP1, 2

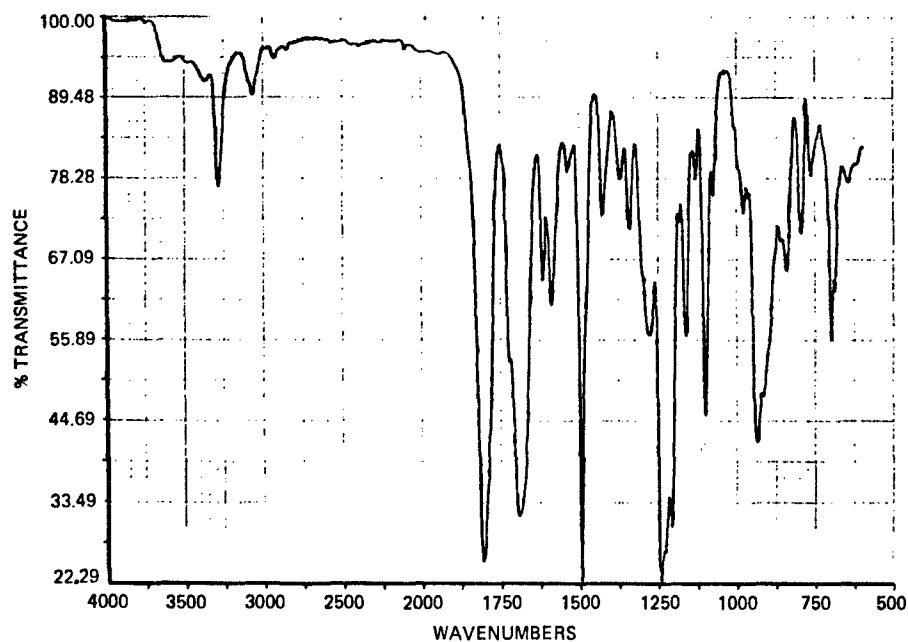


Figure 24. FT-IR spectra of HR6OOP-Mod A (M1126-46).

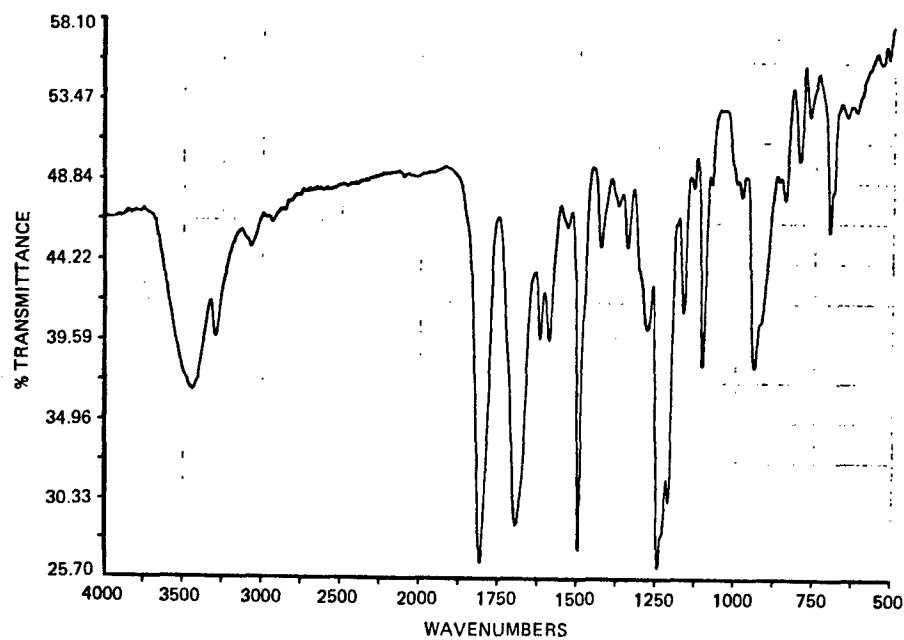


Figure 25. FT-IR spectra of HR6OO-Mod A (M1126-84).

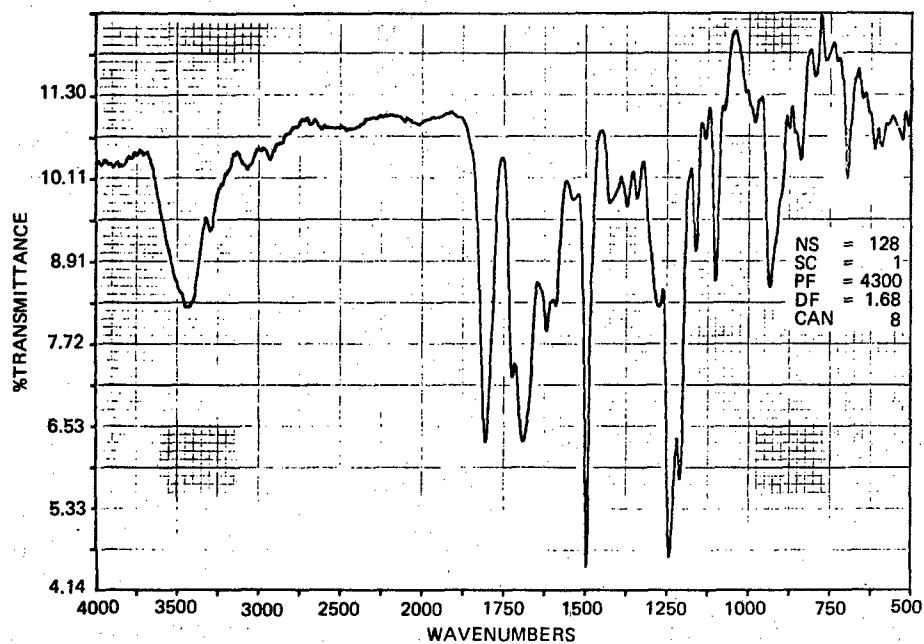


Figure 26. FT-IR spectra of HR6O2P-Mod A (M1126-77B).

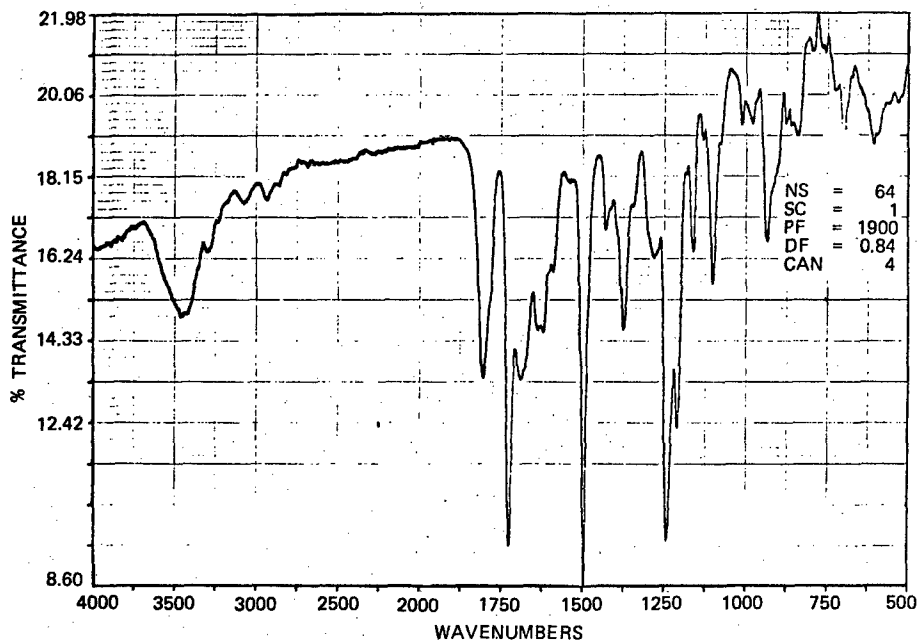


Figure 27. FT-IR spectra of HR6O3P-Mod A (M1126-80).

TABLE 8. PROPERTIES OF NEAT HR60XP MOD-A OLIGOMER

Oligomer	Lot Number	m.p. °C	FTIR Absorbance Spectra-Weight Ratios			Molecular Weight GPLC		DSC MAX*	T _g °C	Post Cure
			Isoimide	Imide	Amic Acid	Mw	Mn			
HR600P	M1126-46	185	1.00	0.12	0.05	2571	1418	227	370	a
									386	b
									397	c
	M1126-84	170	1.00	0.05	0.03	—	—	214	—	—
HR602P	M1126-77B	202	1.00	0.15	0.07	4241	1873	263	339	a
HR603P	M1126-80	218	1.00	1.03	0.02	5237	2703	253	358	a

*Heating rate—10°C/Min N₂

a = 8 hours at 600°F in air

b = 8 hours at 600°F plus 4 hours at 700°F in air

c = 8 hours at 600°F plus 16 hours at 700°F in air

and 3 of HR600P-Mod A. Figures 28-31 depict the differential scanning calorimetry (DSC) curves for these oligomers. These curves appear to indicate two overlapping exotherms. This may be explained by the fact that there are two distinct processes taking place simultaneously during the cure. Further work is required to explain these curves. Figures 32-34 depict the chromatograms obtained by gel permeation chromatography obtained for these oligomers. The molecular weight distribution is shown as well as the various components of the oligomers.

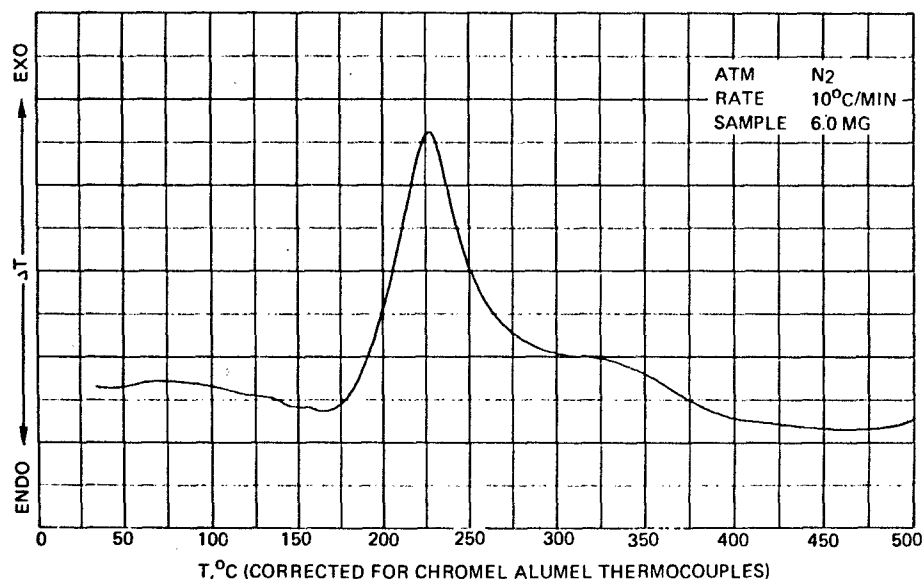


Figure 28. Differential scanning calorimetry (DSC) of HR600P-Mod A (M1126-46).

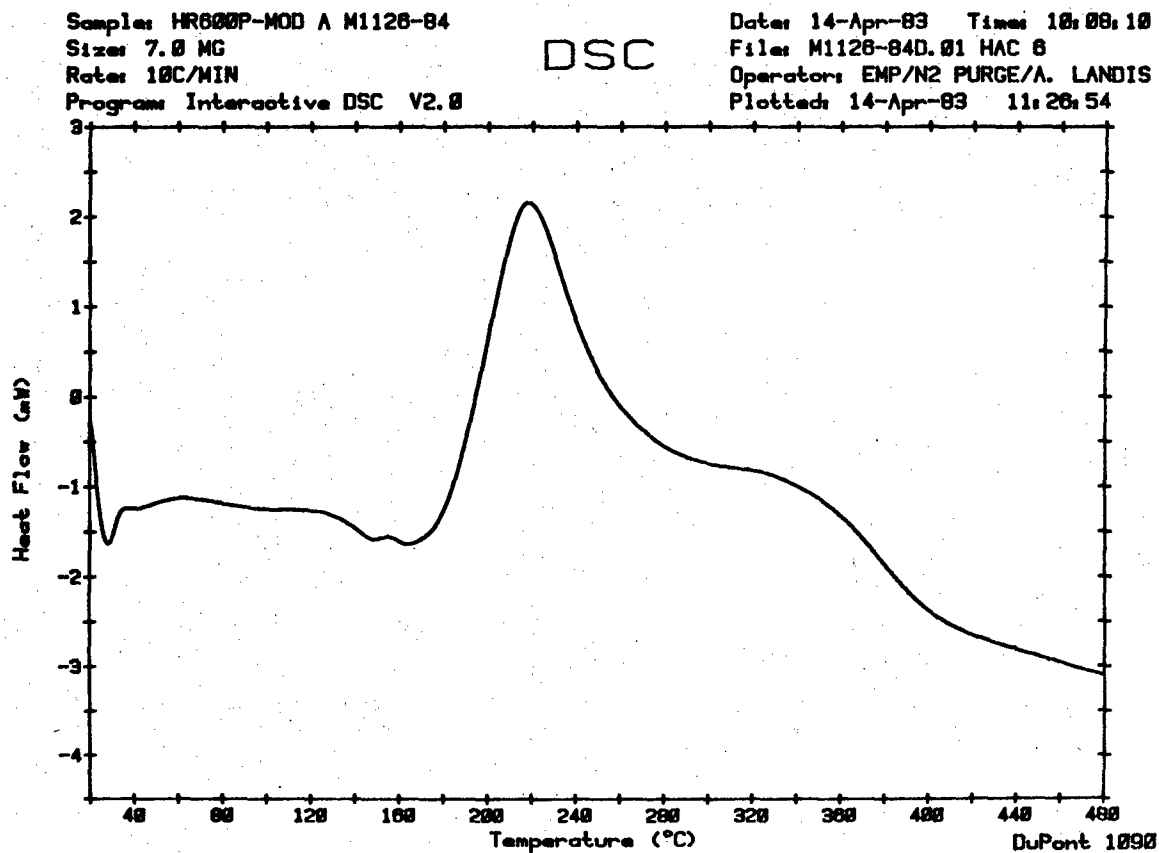


Figure 29. Differential scanning calorimetry (DSC) of HR600P-Mod A (M1126-84).

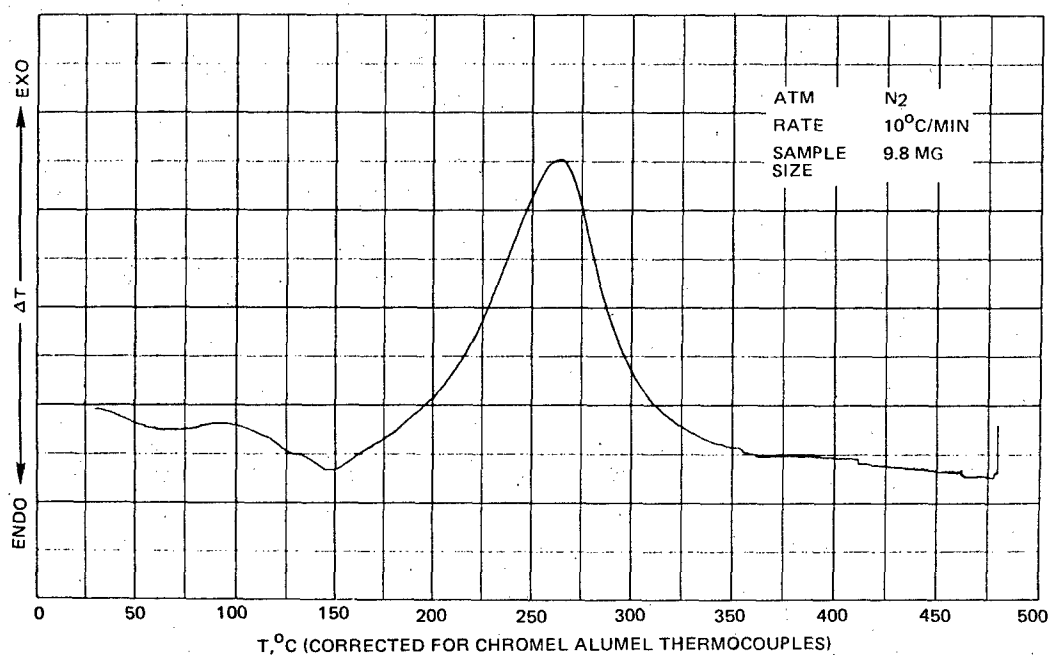


Figure 30. Differential scanning calorimetry (DSC) of HR602P-Mod A (M1126-77B)

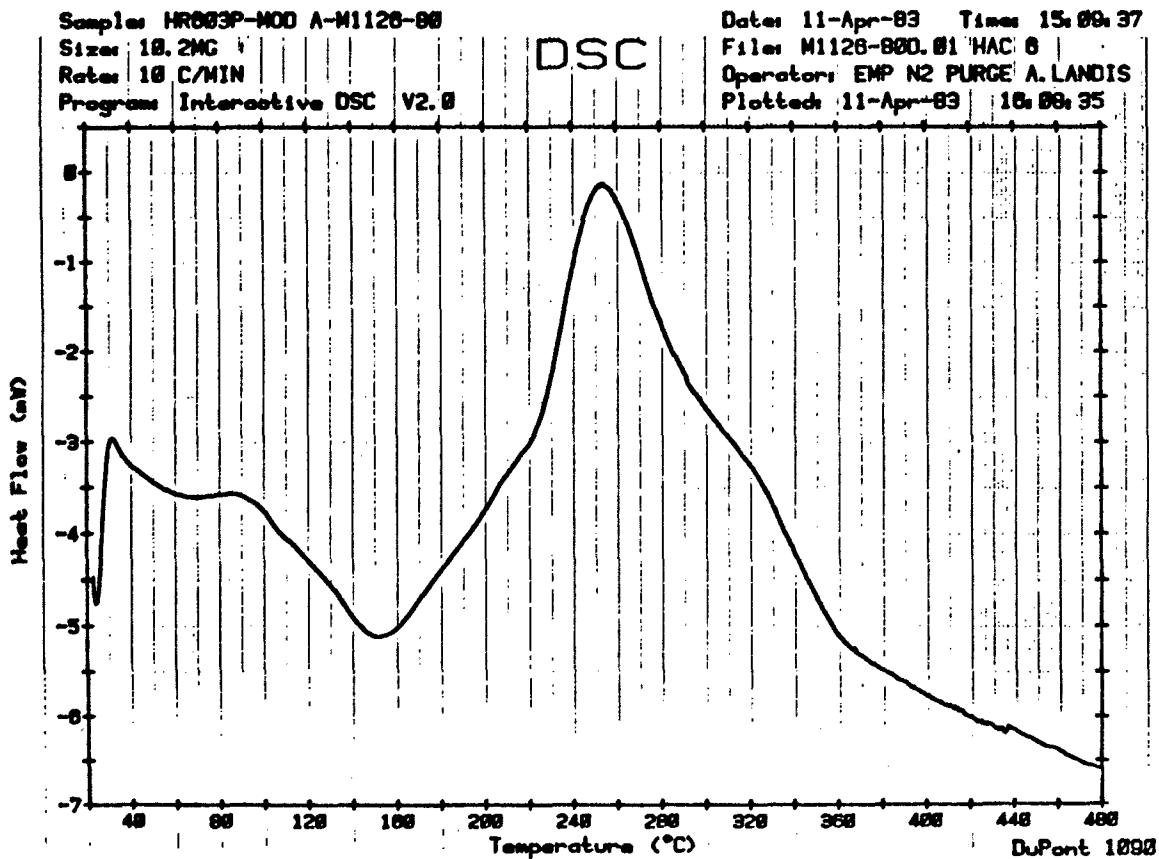


Figure 31. Differential scanning calorimetry (DSC) of HR603P-Mod A (M1126-80).

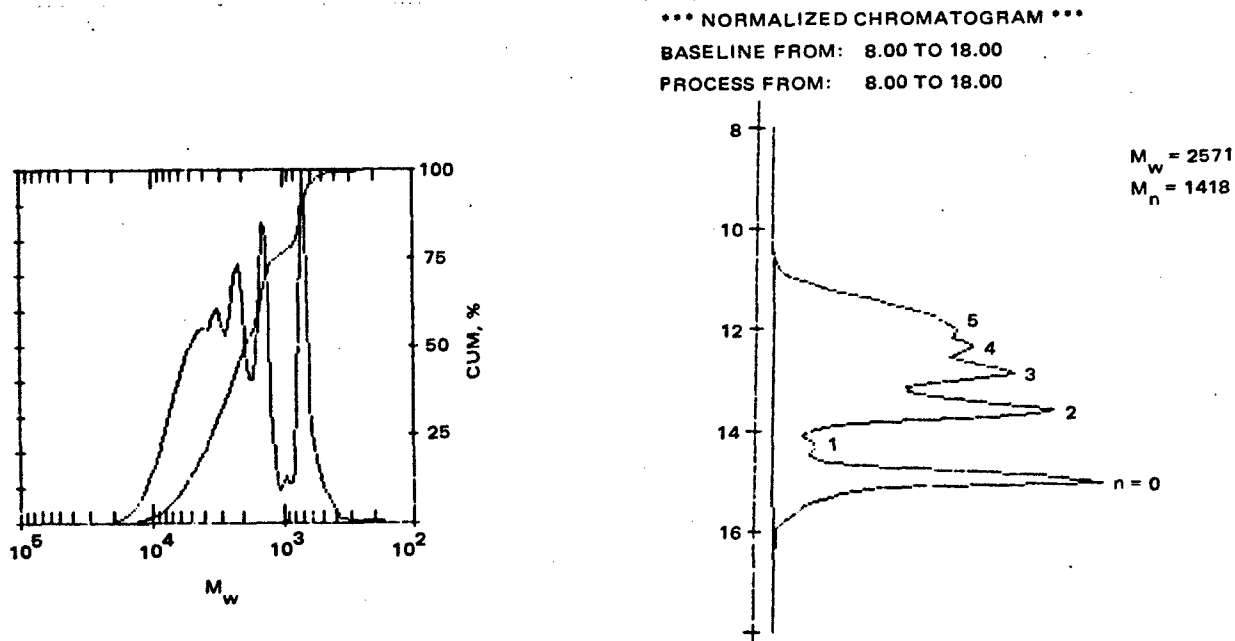


Figure 32. GPC of HR600P Mod A (M1126-46).

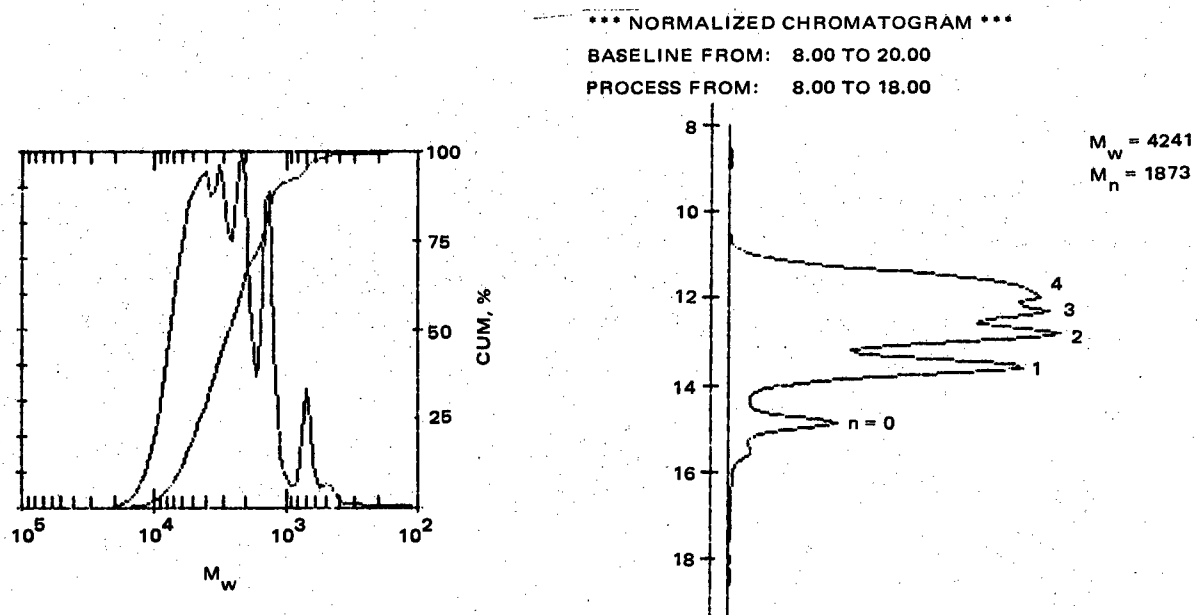


Figure 33. GPC of HR602 Mod A (M1126-77B).

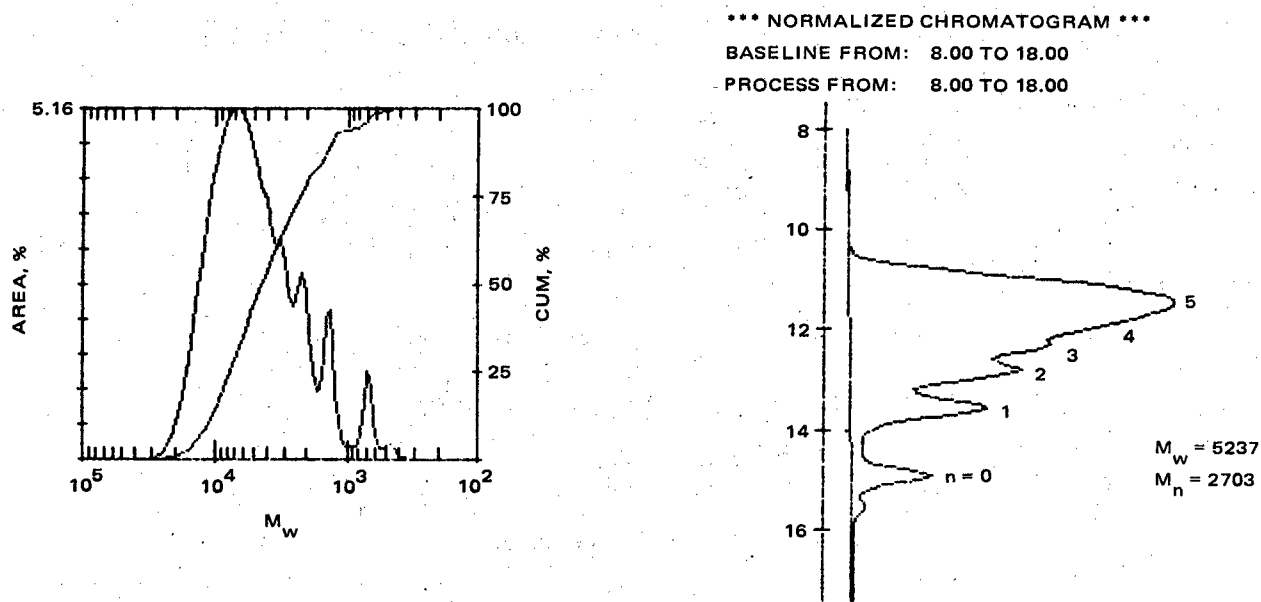


Figure 34. GPC of HR603P Mod A (M1126-80).

3.0 EXPERIMENTAL PROCEDURES

GENERAL DATA

Infrared spectra were recorded on a Nicolet MX-1 Fourier transform spectrometer. Proton magnetic resonance spectra were recorded on either a Varian EM-360L spectrometer or a Varian FT 80-A Fourier transform spectrometer. Carbon magnetic resonance and 250-MHz proton magnetic resonance spectra were obtained using a Bruker WM-250 Fourier transform spectrometer. Mass spectral analyses were performed using a Finnigan OWA/1000 GC-MS spectrometer equipped with a 30-meter SE-54 fused silica capillary, I.D. #0.25 mm. Microanalytical services were provided by Galbraith Laboratories, Inc., Knoxville, Tennessee and MicAnal Organic Microanalysis, Tucson, Arizona. Thermogravimetric-Mass Spectrometric (TGA-MS) analyses were performed by Systems Research Laboratories, Inc., Dayton, Ohio.

Differential Scanning calorimetry (DSC), thermogravimetry (TGA) and thermomechanical analyses (TMA) were performed on both DuPont model 990 and model 1090 thermal analysis systems.

High performance liquid chromatography (HPLC) and Gel permeation chromatography (GPC) were performed using a Beckman Model 345 ternary liquid chromatographic system. HPLC separations employed on Ultrasphere-ODS reverse phase column. GPC separations were accomplished with Microspherogel columns. Both types of columns were supplied by Beckman Instruments.

The three major monomers, APA, APB, and BTDA were purchased from Gulf Oil Chemicals Co. and were further purified before use. APA was redistilled under high vacuum (less than one torr) at which pressure the distillation took place under 110°C, and APB was distilled under high vacuum (less than 25 microns) using the Kugelrohr distillation apparatus. It should be noted that both APA and APB were high quality monomers before purification and the purification was performed to ensure a uniform quality. The dianhydride monomer BTDA as received was also polymer grade. However, it was contaminated with a small amount of free carboxylic acid (1-2 percent). In order to convert the free acid to the anhydride, BTDA was heated to above its melting point and allowed to resolidify. Tetrahydrofuran was reagent grade and distilled from calcium hydride before use. N,N'-dicyclohexylcarbodiimide was the highest grade obtainable (99+ percent). The other solvents, dioxane, isopropyl alcohol and hexane were anhydrous reagent grade.

HR600P Acetylene-Terminated Isoimide Oligomers

1 Percent Excess DCC Added at 5°C, THF Solvent, 7 Percent Solids Content (M1126-10)

A slurry of powdered benzophenonetetracarboxylic dianhydride (BTDA) (58.65 grams, 0.1821 mole) in 500 ml of anhydrous tetrahydrofuran (THF) was placed in a 2-liter three-necked round-bottom flask fitted with a Tru-bore stirrer, an additional funnel and a Claisen adaptor fitted with a thermometer and a drying tube. A solution of 1,3-bis(3-aminophenoxy)benzene (APB) (26.59 grams, 0.09106 mole) in 200 ml of THF was added drop-by-drop, over a 45-minute period to the slurry, at 18°C. At the end of the addition, the temperature had risen to 24°C. After the solution was stirred for an additional 30 minutes, a solution of 3-aminophenylacetylene (APA) (21.31 grams, 0.1821 mole) in 200 ml of THF was added. The solution was stirred for two hours and a 20-ml aliquot was removed and added to 100 ml of hexane to precipitate the amic acid. The amic acid was dried and saved for future reference (M1126-10A). The clear light amber solution was cooled at 5°C and a solution of N,N'-dicyclohexylcarbodiimide (DCC) (76.5 grams, 0.368 mole or a 1 percent excess) in 500 ml of THF was added over one hour while the pot temperature was maintained at below 10°C. The N,N'-dicyclohexylurea (DCU) precipitated during the course of addition. The reaction mixture was stirred for 16 hours and the DCU filtered off. The filtrate was concentrated to 400 ml and cooled in the refrigerator for several hours. An additional small amount of DCU precipitated and was filtered off (about 2 grams). The oligomer was isolated by pouring 120 ml of the filtrate in a blender containing 375 ml of hexane. This was repeated until all the concentrate had been treated in this manner. The bright yellow oligomer was filtered and air dried. The oligomer was then dispersed in 1.5 liters of isopropyl alcohol, filtered, washed with hexane, and dried in a shallow tray in an air circulating oven at 71°C for 30 minutes. The oligomer was finally dried at 85-95°C for two hours under vacuum (about 10^{-1} torr), in a rotary film evaporator. The product (M1126-10B) weighed 96 grams; mp 150-160°C.

5 Percent DCC Added at Ambient, THF Solvent, 10 Percent Solids Content (K1543-138)

A 2-liter, three-necked flask was fitted with a heating mantle, a Tru-bore stirrer, an addition funnel and a reflux condenser with a drying tube. The flask was charged with benzophenonetetracarboxylic dianhydride (BTDA) (58.65 grams, 0.1822 mole) and 500 ml of THF. A solution of 1,3-bis(3-aminophenoxy)benzene (APB) (26.59, 0.09107 mole) in 250 ml of THF was added drop-by-drop over a 45-minute period to the slurry, heated under reflux. After the addition of APB, the solution was heated under reflux for an additional hour. Then a solution of 3-aminophenylacetylene (APA) (21.31 grams, 0.1822 mole) in 150 ml of THF was added. The solution was heated for two additional hours and cooled to ambient temperature. Two-thirds of the total volume was concentrated to 300 ml on the rotary evaporator. The amic

acid was precipitated in several portions by adding each 85-ml portion to 375 ml of hexane in a blender. This process was continued until all the amic acid had been precipitated in this way. The amic acid (82 grams), was air dried and identified as K1543-138. The remainder one-third of the amic acid in solution was converted to the isoimide by a drop-by-drop addition of a solution of N,N'-dicyclohexylcarbodiimide (DCC) (26.5 grams, 0.1274 mole, 5 percent excess) in 100 ml of THF at room temperature. The mixture was stirred for 16 hours and filtered. The isoimide oligomer was isolated in several portions by pouring each 100-ml portion of the filtrate into 375 ml of hexane in the blender. The oligomer was filtered, washed with hexane, dispersed in isopropyl alcohol at 45°C for 15 minutes and then filtered. The solid was dried in a forced air oven at 71°C for one hour and then in the rotary evaporator at 80-90°C for two hours under vacuum. The yellow product (29 grams) was identified as K1543-137A and had a melting point of 150-160°C.

1 Percent Excess DCC Added at Ambient, THF Solvent, 10 Percent Solids Content (M1126-1)

A 2-liter, three-necked flask was fitted with a Tru-bore stirrer, an addition funnel and a Claisen adaptor fitted with a thermometer and a drying tube. The flask was charged with BTDA (58.65 grams, 0.1821 mole) and 500 ml of THF. A solution of APB (26.59 grams, 0.09106 mole) in 200 ml of THF was added drop-by-drop to the mixture (while being constantly stirred) over 30 minutes, at ambient temperature. The solution was stirred for another 45 minutes, treated with a solution of APA (21.31 grams, 0.1821 mole) in 100 ml of THF, stirred for another hour and finally treated with a solution of DCC (76.5 grams, 0.368 mole, 1 percent excess) in 200 ml of THF. The temperature went from 22°C to 34°C. After a short induction period, precipitation of N,N'-dicyclohexylurea (DCU) ensued. The mixture was stirred for 16 hours and filtered. The filtrate was concentrated to one-half its volume on the rotary evaporator. Upon filtering the concentrate, very little additional DCU was recovered.

The oligomer was isolated by pouring about 100 ml of the solution into 350 ml of hexane in a blender. The process was continued until all the filtrate had been treated in this manner. The product was dried in the rotary evaporator at 85-95°C. A yield of 96 grams was obtained; mp 150-160°C.

5 Percent Excess DCC Added At Ambient, THF Solvent, 9 Percent Solids Content, (M1126-3)

A 2-liter, three-necked flask was fitted with a Tru-bore stirrer, an addition funnel and a Claisen adaptor fitted with a thermometer and a drying tube. The flask was charged with BTDA (58.65 grams, 0.1821 mole) and 500 ml of THF. A solution of APB (26.59 grams 0.09106 mole) in 200 ml of THF was added drop-by-drop to the stirred slurry at room temperature, over 35 minutes. After the reaction mixture was stirred for 1.5 hours, a solution of 3-aminophenylacetylene (21.31 grams, 0.1821 mole), in 200 ml of THF was added. The solution

was stirred for an additional 1.5 hours and treated with a solution of DCC (79.5 grams, 0.3824 mole) in 200 ml of THF by a drop-by-drop addition, over 15 minutes. After about one-third of the DCC solution had been added, precipitation of DCU commenced. The temperature during the course of the addition of DCC went from 22° to 34°C. The mixture was stirred for 16 hours and filtered. The filtrate was concentrated to approximately 450 ml on the rotary film evaporator and then filtered again to remove trace amounts of DCU. The oligomer was then isolated by pouring about 100 ml of the filtrate into about 350 ml of hexane in a blender. This process was repeated until all the filtrate had been treated in this manner. The combined batches of product were isolated by filtration. The solid was washed with isopropyl alcohol, stirred in fresh isopropyl alcohol and filtered again. The solid was dried for 45 minutes in an air circulating oven at 71°C and finally in the rotary evaporator at 90–95°C for two hours. The yield was 96 grams; mp 150–160°C (M1126–4).

1 Percent DCC, Added at Below 15°C, Dioxane Solvent, 9 Percent Solids Content (M1126–22)

A 2-liter, three-necked, round-bottom flask was fitted with a Tru-bore stirrer, an addition funnel and a Claisen adapter fitted with a thermometer and a drying tube. The flask was charged with BTDA (40.00 grams, 0.1242 mole) and anhydrous dioxane (350 ml). A solution of APB (18.14 grams, 0.06211 mole) in 150 ml of dioxane was added drop-by-drop to the slurry, over 35 minutes. The solution was stirred for 0.5 hour more, and then a solution of APA (14.53 grams, 0.1242 mole) in 100 ml of dioxane was added. The solution was stirred for an additional hour and then a solution of DCC (52.19 grams, 0.2509 mole, 1 percent excess) in 250 ml of dioxane (250 ml) was added, the reaction temperature being kept at 12–14°C by external cooling. After the addition, the reaction mixture was stirred for 16 hours at room temperature and filtered to remove the DCU. The filtrate was concentrated to 275 ml on the rotary evaporator and the concentrate cooled to 0–5°C for several hours and filtered again. Only trace amounts of DCU was removed (about 0.3 grams). The oligomer was isolated in several portions by pouring each 60-ml portion of the filtrate into about 350 ml of isopropyl alcohol in a blender. The oligomer was isolated by filtration, air dried for 30 minutes and then vacuum dried at 80–90°C for two hours. The product (M1126–22A) weighed 68 grams and had a volatile content of 7.9 percent (determined by heating a sample for 15 minutes at 250°C without vacuum. Even after prolonged drying for 72 hours at 15 microns at 80°C, the volatile content was still 5.8 percent.

Large Scale Synthesis, 1 Percent Excess DCC Added at Below 4°C, THF Solvent, 12 Percent Solids Content (M1126–24)

A 12-liter, three-necked, round-bottom flask was fitted with a cooling bath, a Tru-bore stirrer, a pressure-equalizing additional funnel and a Claisen adapter fitted with a thermometer and a drying tube. The flask was charged with BTDA (340.0 grams, 1.056 moles) and THF

(3.0 liters). A solution of APB (154.2 grams, 0.5280 mole) in one liter of THF was added over a two-hour period to the slurry, starting at 20°C. The temperature at the end of the addition was 24°C. After the reaction mixture was stirred for 30 minutes, a solution of APA (123.6 grams, 1.056 moles) in 500 ml of THF was added over 15 minutes. The solution was stirred for two hours, cooled to -5°C, and treated with a solution of DCC (443.6 grams, 2.133 moles, 1 percent excess) in one liter of THF by dropwise addition for 30 minutes, the temperature being kept below 4°C during the addition. The reaction mixture was stirred for 16 hours at ambient temperature and the DCU filtered off. The filtrate was concentrated to 1700 ml and cooled for 24 hours at 0-5°C. The solution was then filtered to yield several more grams of DCU. The filtrate was worked up in 100-ml portions by adding each portion to about 350 ml of isopropyl alcohol in a blender. The precipitated oligomer was isolated by filtration, washed with hexane and air dried for two hours in a shallow tray. It was then dried in a vacuum (10^{-1} torr) at 80°C to yield 610 grams (M1126-24). Drying a portion of the product for 24 hours at 100°-124°C in a vacuum at 5 microns gave a product having a volatile content of 2.2 percent (determined by heating a sample at 250°C for 30 minutes without vacuum).

1 Percent Excess DCC Added at -10°C, THF Solvent, 22.5 Percent Solids Content (M1126-29)

A one-liter, three-necked, round-bottom flask was fitted with a Tru-bore stirrer, a pressure equalizing addition funnel and a Claisen adapter fitted with a thermometer and a drying tube. The flask was charged with BTDA (68.0 grams, 0.2112 mole) and anhydrous THF (300 ml). A solution of APB (30.83 grams, 0.1056 mole) in 100 ml of THF was added drop-by-drop over 30 minutes to the slurry. The temperature rose from 23° to 28°C. A solution of APA (24.71 grams, 0.2112 mole) in 50 ml of THF was added. The pot temperature rose to 33°C. After stirring the solution for 1.5 hours, the solution was cooled to -10°C and a solution of DCC (88.7 grams, 0.427 mole, 1 percent excess) in 100 ml of THF was added over 15 minutes. The temperature rose to 4°C. The reaction mixture was stirred at ambient temperature for 16 hours. The slurry was filtered to remove the DCU and the filtrate cooled for two hours at 0-5°C to precipitate additional DCU (about 1-2 grams), which was filtered off. The filtrate was divided into two roughly equal parts. The first portion was used to precipitate the oligomer from hexane, and the second from isopropyl alcohol. In both cases, the precipitation was effected by adding 100 ml of the filtrate to approximately 375 ml of the solvent. Both batches of oligomers were isolated by filtration, then air dried and finally vacuum dried (10^{-1} torr) in the rotary film evaporator at 80-90°C. A yield of 44 grams (M1126-29A) was obtained from the hexane precipitation process and 45 grams (M1126-29B) was obtained from the isopropyl alcohol precipitation process. The volatile content of M1126-29A was 3.0 percent and of M1126-29B, 2.1 percent. The volatile content was determined by heating a sample at 250°C for 30 minutes without vacuum.

Large Scale Synthesis, 1 Percent Excess DCC Added at +10°C, THF Solvent, 23.6 Percent Solids Content (M1126-39)

A 12-liter, three-necked, round-bottom flask was fitted with a heating mantle, Tru-bore stirrer, a pressure-equalizing addition funnel, and a Claisen adapter fitted with a thermometer and a reflux condenser with a drying tube. The flask was charged with BTDA (544 grams, 1.689 moles) and anhydrous THF (2.4 liters). The slurry was heated to 45°C and a solution of APB (246.7 grams, 0.8447 mole) in 800 ml of THF was added drop-by-drop during 45 minutes, the temperature being kept at 40-45°C. At the end of the addition, all the solids were in solution. The solution was stirred for an additional 30 minutes at 40°C. A solution of APA (197.7 grams, 1.689 mole) in THF (200 ml) was then added over 15 minutes, the pot temperature being kept at 40-45°C. The solution was stirred at ambient temperature for two hours. A 10-ml aliquot solution was withdrawn from the reaction mixture and the amic acid was precipitated in hexane and dried and identified as M1126-39A. After cooling the reaction mixture to 6°C, a solution of DCC (710 grams, 3.413 moles, 1 percent excess) in 800 ml of THF was added drop-by-drop at 8-11°C. The mixture was stirred for 30 minutes at this temperature. A 10-ml aliquot sample was withdrawn and the oligomer was precipitated in hexane, and dried. This sample was identified as M1126-39B. In a similar manner, another 10-ml aliquot portion was withdrawn and worked-up in isopropyl alcohol. This sample was identified as M1126-39C. The cooling bath was removed and the reaction mixture was stirred at ambient temperature for 16 hours. The slurry was cooled to 3°C to maximize the precipitation of DCU and filtered. A total of 5.1 liters of filtrate was obtained, representing a solid content of about 20 percent. The filtrate was divided into three approximately equal portions (1700 ml each), and each portion was added to 6.8 liters of isopropyl alcohol in a 12-liter, three-necked, round-bottom flask equipped with a Tru-bore stirrer and an addition funnel. The finely-divided light yellow slurry was filtered and the solid was dried in a vacuum oven at 45°C for 16 hours, and finally at 70°C in vacuum for two hours. The sample is identified as M1126-39D (790 grams, 85 percent of theory) had a softening temperature of 155°C and a volatile content of 1.3 percent (determined by heating a weighed sample at 250°C for 30 minutes without vacuum).

HR602P Acetylene-Terminated Isoimide Oligomers

1 Percent Excess DCC Added at 40°C, THF Solvent, 13 Percent Solids Content (M1126-12)

A two-liter, three-necked, round-bottom flask was fitted with a Tru-bore, an addition funnel, and a Claisen adapter fitted with a thermometer and a drying tube. The flask was charged with BTDA (57.64 grams, 0.1790 mole) and anhydrous THF (500 ml). A solution of APB (34.84 grams, 0.1193 mole) in 250 ml of THF was added drop-by-drop over 45 minutes to the slurry, at 18°C. After stirring for an additional 30 minutes, the mixture was treated with a

solution of APA (13.96 grams, 0.1193 moles) in 100 ml of THF. A 20-ml aliquot of the reaction solution was withdrawn and mixed with hexane to precipitate the amic acid (M1126-12A). The reaction mixture was cooled to 4°C and a solution of DCC (75.2 grams, 0.362 mole, 1 percent excess) in 500 ml of THF was added drop-by-drop at a temperature below 4°C. The reaction mixture was then stirred at ambient temperature for 16 hours. After the DCU precipitate was filtered off, the filtrate was concentrated to 350 ml using the rotary evaporator and stored for 24 hours at 0-5°C. The additional amount of DCU which precipitated was filtered off.

The filtrate was worked-up in 100-ml portions by pouring each portion into 375 ml of hexane in a blender. A total of 1.8 liters of hexane was used to precipitate the oligomer in this manner. The combined batches of the oligomer were isolated by filtration, air-dried for 30 minutes, dispersed in isopropyl alcohol for four hours, filtered again, air-dried for 16 hours in a shallow tray, and finally vacuum-dried at 85-90°C/10⁻¹ torr in the rotary evaporator for two hours. The product (M1126-12B), weighed 99.5 grams and melted at 165-170°C; its Fourier transform infrared spectrum showed the characteristic absorptions due to the acetylene end groups and the isoimide ring structure.

1 Percent Excess DCC Added At 0°C, THF Solvent, 19 Percent Solids Content (M1126-31)

A one-liter, three-necked, round-bottom flask was fitted with a Tru-bore stirrer, a pressure equalizing addition funnel and a Claisen adapter fitted with a thermometer and drying tube. The flask was charged with BTDA (57.64 grams, 0.1790 mole) and anhydrous THF (250 ml). A solution of APB (34.84 grams, 0.1193 mole) in 125 ml of THF was added drop-by-drop to this slurry, over 45 minutes. The pot temperature rose from 30° to 38°C. The solution was stirred for one hour after the addition and treated with a solution of APA (13.96, 0.1193 mole) in 50 ml of THF. The reaction mixture was then stirred for 45 minutes, and cooled to -5°C, before a solution of DCC (75.2 grams, 0.364 mole, 1 percent excess) in 100 ml of THF was added over 15 minutes; the pot temperature being maintained at 0°C. The resulting slurry was stirred for 16 hours and then the DCU filtered off. Further cooling the filtrate cooled for 24 hours at 0-5°C yielded only an additional small amount of DCU (about 0.25 gram). The filtrate was divided into two parts. In one case, hexane was used as a precipitating solvent, and in the second case, isopropyl alcohol was used. The process was precipitated in 100-ml portions by adding each portion to 350 ml of the precipitating solvent in a blender. In each case, the solid was filtered, air-dried at 71°C (160°F) for 30 minutes and finally dried under vacuum (10⁻¹ torr) for two hours in the rotary evaporator. The product (M1126-31A), precipitated from hexane weighed 45 grams, and had a softening point of 170°C and a volatile content of 6.3 percent. The volatile content was determined by heating a sample at 250°C for 30 minutes. The oligomer (M1126-31B), precipitated with isopropyl alcohol, weighed 39 grams, and had a softening point of 170°C, and a volatile content of 3.1 percent.

HR605P Acetylene-Terminated Isoimide Oligomers

1 Percent Excess DCC Added at Below 9°C, THF Solvent, 8 Percent Solids Content (M1126-14)

A two-liter, three-necked, round-bottom flask was fitted with a Tru-bore stirrer, an addition funnel and a Claisen adapter fitted with a thermometer and a drying tube. The flask was charged with BTDA (56.65 grams, 0.1759 mole) and anhydrous THF (500 ml). A solution of APB (42.82 grams, 0.1466 mole) in 300 ml of THF was added drop-by-drop to the slurry, at 18°C, over 45 minutes. The solution was stirred for an additional 30 minutes, and treated with a solution of APA (6.86 grams, 0.0586 mole) in 100 ml of THF. The stirring was continued for an additional two hours. A 10-ml aliquot of the reaction solution was withdrawn and added to hexane to precipitate the amic acid. (M1126-14A). The reaction mixture was cooled to 4°C and a solution of DCC (73.9 grams, 0.355 mole, 1 percent excess) in 500 ml of THF was added drop-by-drop over one hour, the pot temperature being maintained below 9°C throughout the addition. Stirring was continued at ambient temperature for 16 hours. The mixture was filtered and the filtrate concentrated to 375 ml on the rotary evaporator. The concentrate was cooled to 0-5°C for 24 hours to allow precipitation of a second crop of DCU. The filtrate was worked-up in 100-ml portions by pouring each portion to 300 ml of hexane in a blender. The oligomer was isolated by filtration, air-dried (1 hour), dispersed in 1.5 liters of isopropyl alcohol, filtered again, air-dried, and then further dried at 80-90°C/0.1 torr in the rotary evaporator. The product (M1126-14B) weighed 97 grams and melted at 175-180°C.

1 Percent Excess DCC Added at 0°C, THF Solvent, 22 Percent Solids Content (M1126-33)

A one-liter, three-necked, round-bottom flask was fitted with a Tru-bore stirrer, a pressure equalizing addition funnel, and a Claisen adapter, fitted with a thermometer and a drying tube. The flask was charged with BTDA (56.65 grams, 0.1759 mole) and anhydrous THF (225 ml). The slurry was warmed to 30°C, and APB (42.82 grams, 0.1466 mole) in THF (150 ml) was added drop-by-drop over 30 minutes. The pot temperature rose to 38°C during the addition. The solution was stirred for 30 minutes and then APA (6.86 grams, 0.05863 mole) in 25 ml of THF was added. The solution was further stirred for one hour, cooled to -5°C, and then treated with a solution of DCC (73.9 grams, 0.3553 mole, 1 percent excess) in 50 ml of THF by drop-by-drop addition; the temperature of the mixture being kept at 0°C. Cooling to -10°C caused gelation but the gel redissolved at higher temperatures. Stirring was continued for 16 hours and the DCU precipitate was filtered off. Cooling the filtrate at 0-5°C for 72 hours yielded a small amount of DCU (0.35 grams) which was filtered off. The filtrate (480 ml) was divided into two parts: one part was mixed with hexane, and the other with isopropyl alcohol. In each case, precipitation was effected in 100-ml portions by adding each portion to 350 ml of the precipitating solvent in a blender. The combined batches of product were

isolated by filtration, air-dried for 16 hours, and finally dried in the rotary evaporator at 70–90°C/0.1 torr for two hours. The oligomer batch precipitated with isopropyl alcohol (M1126–33A) weighed 38 grams, having a softening temperature of 177°C, and a volatile content of 3.8 percent. The oligomer batch precipitated with hexane (M1126–33B), weighed 42 grams, and had a softening temperature of 182°C and a volatile content of 3.0 percent.

HR600P Mod A—Acetylene-Terminated Isoimide Oligomers Made With 4,4'-Oxydianiline (ODA)

1 Percent Excess DCC Added at 10°C, THF Solvent, M1126–46

A two-liter, three-necked, round-bottom flask was fitted with a heating mantle, a Tru-bore stirrer, an addition funnel, and a Claisen adapter fitted with a thermometer, and a reflux condenser protected with a drying tube. The flask was charged with BTDA (150.0 grams, 0.4658 mole) and anhydrous THF (1.0 liter). The mixture was heated to the reflux temperature of THF and stirred vigorously to get as much BTDA in solution as possible. Then the mixture was cooled to 40°C and ODA (46.58 grams, 0.2329 mole) was added in 1-gram portions. The addition took 20 minutes and the temperature was maintained at 40–45°C. At the end of the addition, there was still a small amount of suspended solids. Stirring was continued for 30 minutes and APA (54.5 grams, 0.4658 mole) was added drop-by-drop for 10 minutes. The reaction mixture was heated at reflux for 45 minutes. All the solids dissolved at this point. The solution was cooled to 5°C and treated by a drop-by-drop addition with a solution of DCC (193.8 grams, 0.9409 mole, 1 percent excess) in 200 ml of THF; the temperature being kept between 6° and 11°C. Stirring was continued for one hour and the DCU was removed by filtration. The filtrate (1500 ml) was added drop-by-drop to 6 liters of isopropyl alcohol while being vigorously stirred. The slurry was chilled to 5°C and filtered. The solid was dried at room temperature under vacuum for 16 hours, at 35°C for two hours, and then at 80°C for 16 hours. The product (M1126–46), weighed 202 grams, and had a melting point of 185°C. The volatile content of 0.68 percent was determined by heating a sample at 250°C for 30 minutes.

Large Scale Synthesis, 3 Percent Excess DCC Added at 10°C, THF Solvent

A 12-liter, three-necked, round-bottom flask was fitted with a Tru-bore stirrer, an addition funnel, and a Claisen adapter fitted with a drying tube and a thermometer. The flask was charged with BTDA (644.0 grams, 2.00 moles) and anhydrous THF (4.0 liters). A solution of ODA (200.0 grams, 1.00 mole) in three liters of warm THF (35°C) was added drop-by-drop to the slurry at 25°C, over 1.25 hours. After two-thirds of the solution had been added, most of the suspended BTDA had gone into solution. After the addition of ODA was completed, a negligible amount of BTDA remained in suspension and the pot temperature reached 32°C. The solution was stirred for an additional 30 minutes, and APA (234 grams, 2.00 moles) was

added in one portion. The temperature rose to 39°C at the end of the addition. The solution was stirred for an additional hour, cooled to 8°C and treated by a drop-by-drop addition with a solution of DCC (848.7 grams, 4.12 moles, 3 percent excess) in one liter of THF, over 1.5 hours. The temperature was kept between 8 and 10°C during the addition. The resulting slurry was stirred for 16 hours at 25°C and filtered. The filtrate was concentrated to 5.0 liters on the rotary evaporator, cooled to 0°C and then filtered to remove an additional 5 grams of DCU. The filtrate was worked up in 100-ml portions by pouring each portion into 350 ml of isopropyl alcohol in a blender. This process was repeated until all of the filtrate had been treated. The total volume of the slurry was 22 liters. The slurry was filtered through a large Buchner funnel using Whatman No. 4 filter paper. The product (M1126-84) weighed 920 grams, melted at 170°C, and had a volatile content of 1.1 percent.

HR602P Mod A—Acetylene-Terminated Isoimide Oligomers Made With ODA

3 Percent Excess DCC, Added At Below 10°C, DMAC Solvent

Our results indicated that the use of THF does not give a homogeneous reaction medium in the synthesis of oligomers having degrees of polymerization greater than one. Thus, *N,N'*-dimethylacetamide (DMAC) was used instead in this preparation since it is an excellent solvent for higher molar weight fractions of amic acid from Mod-A. A two-liter, three-necked, round-bottom flask was fitted with a heating mantle, a Tru-bore stirrer, an addition funnel, and a Claisen adapter fitted with a thermometer and a drying tube. The flask was charged with BTDA (89.4 grams, 0.2776 mole) and anhydrous DMAC (500 ml). The solution was warmed to 40°C whereupon all the BTDA went into solution. Then ODA (37.0 grams, 0.1851 mole) in 150 ml was added drop-by-drop over 30 minutes. The solution was stirred for 30 minutes and APA (16.24 grams, 0.1852 mole) was added. The resulting solution was stirred for 30 minutes, cooled to 3°C, and treated by a drop-by-drop addition with a solution of DCC (117.8 grams, 0.5719 mole), in 100 ml of DMAC while the pot temperature was kept below 10°C. The resulting slurry was allowed to stand for 45 minutes and filtered. The filtrate was worked up in 100-ml portions by adding each portion to 350 ml of isopropyl alcohol. A portion of the oligomer was redissolved in THF to give a solution of 20 percent solids content, filtered, and reprecipitated with isopropyl alcohol. This product was dried under vacuum at ambient temperature and then at 80–90°C/0.1 torr in the rotary evaporator. This batch of oligomer (M1126-77B) weighed 19 grams, and had a melting point of 202°C, and a volatile content of 8.6 percent. The other part of the oligomer, which was not treated in this manner, became gummy. No further work was done on that portion.

HR603P Mod-A—Acetylene-Terminated Isoimide Oligomers Made With ODA

3 Percent Excess DCC Added at Below 10°C, DMAC Solvent (M1126-80)

A one-liter, three-necked, round-bottom flask was fitted with a Tru-bore stirrer, a thermometer and a pressure equalizing addition funnel. The flask was charged with BTDA (20.0 grams, 0.06211 mole) and anhydrous DMAC (150 ml). A solution of ODA (9.32 grams, 0.4658 mole) in 100 ml of DMAC was added drop-by-drop over 30 minutes while being continuously stirred. The temperature rose from 25 to 33°C. After the solution was stirred for 30 minutes, APA (3.63 grams) was added. About 20 ml of DMAC was used to rinse the small beaker free of APA which was added to the reaction flask. The solution was stirred for one hour and then cooled to 0°C. A solution of DCC (26.4 grams, 0.1280 mole, 3 percent excess) in 100 ml of DMAC was added drop-by-drop over 15 minutes, while the pot temperature was maintained at 0-10°C. The slurry was stirred at ambient temperature for 16 hours and the DCU was removed by filtration. The filtrate was worked-up in 100-ml portions by adding each portion to 350 ml of isopropyl alcohol in a blender. The oligomer precipitated as a fine yellowish-orange powder, recovered by filtration, dried at ambient temperature under vacuum in a rotary film evaporator, and then further dried for two hours at 80-90°C/10.1 torr. The product (M1126-80) weighed 30 grams, melted at 218°C and had a volatile content of 11.4 percent.

HR605P Mod-A—Acetylene-Terminated Isoimide Oligomers Made With ODA

3 Percent Excess DCC Added at Below 10°C, DMAC Solvent

A one-liter, three-necked, round-bottom flask was charged with BTDA (20.0 grams, 0.06211 mole) and anhydrous DMAC (150 ml). A solution of ODA (10.35 grams, 0.5176 mole) in 100 ml of DMAC was added drop-by-drop over 30 minutes, followed by APA (2.42 grams, 0.02070 mole). The solution was then stirred for an additional 30 minutes, cooled to 0°C and treated with a solution of DCC (26.4 grams, 0.1280 mole, 3 percent excess) in 50 ml of DMAC, added drop-by-drop over 15 minutes. The temperature of the reaction mixture was kept below 10°C. The slurry was stirred at room temperature for 16 hours. Gelation occurred during this period. The gel was insoluble in DMAC or THF.

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